170 | V | D

NEW ZEALAND JOURNAL OF SCIENCE

VOL. 2 NO. 2 JUNE 1959

N S P
R A M
M M
COMMONWEALTH MYCOLOGICAL INSTITUTE
18 AUG 1959

NOTICE TO CONTRIBUTORS

General

Papers published, or offered for publication, elsewhere are not acceptable. Nevertheless, publication elsewhere of an abstract or of an extended summary does not preclude publication in full in this journal.

Typescript

The original and one carbon copy are required, on one side only of foolscap paper, double spaced, with a left-hand margin of at least one inch and a quarter. Reasonably heavy good-quality paper should be used. flimsy paper delays the machine operator and consequently increases the cost of printing.

A brief summary is required, at the beginning of the paper. It should indicate the scope of the paper and give the principal results, and should be suitable for reproduction by abstracting journals as it stands.

All matter to be printed in italic type (e.g., generic and specific names) must be underlined.

Tables

Tabular matter costs more to print than letterpress and should therefore be kept to a minimum, bearing in mind, however, that a well-planned table can take the place of a much greater area of letterpress.

Wherever possible, tables should be arranged to fit upright on the page, not sideways. They will be printed in 8-point type.

All tables, however brief, should be numbered in arabic numerals. Numerous very small tables should be avoided.

Titles should be as brief as possible.

Units of measurement should be placed in parentheses at the head of the column, not in the body of the table. Descriptive notes should be kept to the minimum, and abbreviations used wherever possible. For abbreviations, etc., the usage followed is that of British Standard 1991, Letter Symbols, Signs, and Abbreviations. Part 1. General.

Figures

These are to be numbered consecutively in arabic numerals, regardless of whether they are half-tones (photographs) or line blocks (graphs, etc.). Each must be referred to in the text, and only such figures as are essential to elucidate the text can be published.

The author's name, the title of the paper (abbreviated), and the figure number should be written lightly in soft pencil on the back of each figure.

Photographic prints should be on glossy paper, and may be the same size as or larger than the printed picture. Components of a composite figure should be firmly mounted on white card, and lettered as required A, B, C, etc.

Graphs should preferably be drawn about twice the final size, with the curves evenly inked throughout. Great care should be taken to ensure that all detail, especially lettering, is of such size as to be clearly legible when reduced to the final size. If he wishes, the author may insert lettering in pencil for re-draughting in this office.

If the scale is important, it should be shown on the figure, or, alternatively, the magnification or reduction may be stated in the caption, taking into account the printing reduction.

The figure number should not be given on the figure itself, only in the caption. Captions for all figures should be typed together at the end of the paper.

References

In the text, citations are to be by author's name and year, e.g. "(Brown, 1957)" or " . . . as stated by Brown (1957)". The list of references at the end of the paper is to be arranged in alphabetical order of authors' names. Titles of papers cited may be included or omitted; if included, all words other than conjunctions, pronouns, and prepositions are to have capital letters. Titles of periodicals are to be abbreviated in accordance with the "World List of Scientific Periodicals", 3rd ed. 1952. The title of the periodical and the volume (and part) number are to be underlined for italics, but not the page number(s). Titles of books are to be inverted commas and not underlined; the name and location of the publisher are to be given. For arrangement, punctuation, etc., of references, see examples in this issue.

NEW ZEALAND
JOURNAL OF SCIENCE

Department of Scientific and Industrial Research, Wellington.
Editor*: *Mabel Rice

VOL. 2 JUNE 1959 NUMBER 2

A STUDY OF HOME RANGE IN A FERAL GOAT HERD

By THANE RINEY and GRAEME CAUGHLEY, New Zealand Forest Service, Wellington, New Zealand

(Received for publication, 5 February 1959)

Summary

The movements of a small population of free-ranging feral goats (*Capra hircus*) were studied for sixteen months, advantage being taken of individual natural markings adequate for identification of each animal.

In the winter, adult females went into the forest, leaving the nanny-kid herd in the more open area, where the study was concentrated. This was an area common to all nanny and kid home ranges, and more than 90% of all observations were made in this herd range, which was 1,050 yards at its widest diameter. The herd range consisted of three high-use areas surrounded by areas of less use.

In the nanny-kid herd, two groupings were recognized—the family group, and the larger more temporary associations formed within the herd. The herd was never observed all together at any one time. There was no antagonism between groups or associations, and although some aggressive behaviour occurred among billies, no signs of dominance or leadership emerged.

The boundary of a herd range appears to be more in the nature of a band or zone than a line, and in this area it is apparently influenced by the availability of cover. Relations between sheep and goats do not appear to affect boundary formation and shooting has not been intensive enough to permanently alter the shape of the herd range.

The nanny-kid herd is considered the part of the population most suitable for the application of management and control measures.

INTRODUCTION

Dice (1952) has elaborated the concept that "The precise place in the ecosystem at which each individual plant and animal is situated in relation to its neighbours is of considerable significance in the organization of the community", and it is with this concept in mind that the present

study has been pursued. Although the general definition of home range furnished by Dice (1952) has been accepted here ("The area over which an individual animal habitually travels while engaged in his usual daily activities may be called his home range"), the specific consideration in the present study has been the yearly home range of a small herd of feral nanny and kid goats (*Capra hircus*), each individually recognizable. Individual characteristic colour patterns, recognizable at long range, rendered it unnecessary to catch and mark the animals. As pointed out by Amschler (1929), the domestic goat is derived from three wild species, *C. falconeri, C. prisca,* and *C. aegagrus,* which he separates principally by their characteristic horns. The goats in the present study are apparently related most closely to the ancestral *C. prisca* species.

METHODS

As the goats had a variety of markings, a notebook form was designed showing the outline of a goat from both sides, front, and rear, and the colour and pattern of each goat was filled in on one of these forms (Fig. 1). Goats could thus be identified at distances up to eight hundred yards using 7 × 50 binoculars, but the majority were identified from distances of less than five hundred yards. The thirty-seven goats recorded in this way include all the resident nannies and kids in the area and most of the temporarily resident billies. Most observations were made from three vantage points so that it was seldom necessary to change position to keep moving goats in view. Before any decision was made as to the relationships between members of an aggregation of goats, the aggregation was observed for at least half an hour.

To supplement records of direct observations on the distribution of goats in different habitats, one sample line of forty stations was used on which faeces were counted on mil-acre plots spaced ten paces apart. This is a modification of the technique described by Riney (1957).

Observations were carried out at intervals during sixteen months between January 1957 and April 1958, to record movements at all seasons.

The area studied is in the Rimutaka Range, eight miles east of Upper Hutt in the North Island of New Zealand. It consists of marginal sheep-farming country bordering on forest. The habitat consists of second-growth scrub, unimproved pasture, forest, fern, and bare ground. In addition to goats, Romney sheep and occasional deer and feral pigs use part of the area.

SOCIAL ORGANIZATION

Since the social organization of the goat herd has a considerable influence on the boundaries of the individual home ranges, it is appropriate to describe briefly the basic organization of this goat community.

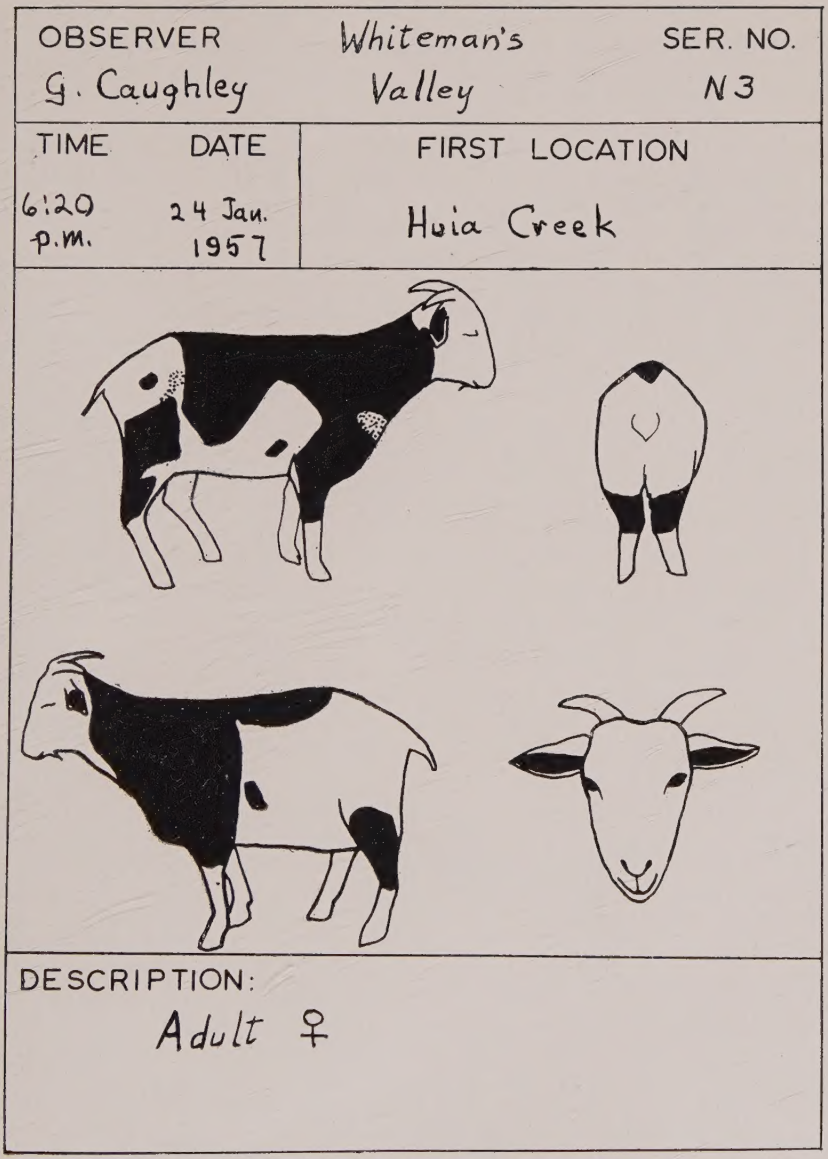


FIG. 1.—Sample page from field notebook used for recording individual colour patterns for identification of each animal.

A seasonal segregation of sexes occurs. During the winter the adult males live in the forest and at this time it is rare to see a billy on the forest margin. Thus the only study area chosen was essentially one occupied by the nannies and juveniles and used by the billies only during the summer months.

Two different kinds of grouping are recognizable. The basic unit of the population is the family group of a nanny and her last offspring. A typical family group consists of a nanny and either one or two kids. In this area, no female was seen with kids of more than one age consistently associating with her. The second kind of grouping is usually larger; it consists of a number of goats associating together as they feed, travel, rest, or mate. These associations are continually forming, breaking up, splitting, and amalgamating. Goats drift away from or move into associations without any observable signs of recognition or of any antagonism. They apparently recognize and accept neighbouring goats with which they are temporarily and intermittently associated. In this area, associations other than family groups varied in size from two to fourteen, an analysis of twenty-seven of these associations giving an average of 3·8 goats in each. One case only was observed of goats entering the area for the first time. In February 1957, when a family group new to the area tried to join an association of three other goats, it was obvious that the three goats were somewhat disturbed by the new arrivals. This was evident from their extreme curiosity but without any associated aggressive behaviour. The new arrivals seemed indifferent, and when they were observed twenty days later, they were a completely integrated component of the herd.

These two groupings are units of a larger unit of the population, referred to in this paper as the herd. This is the whole nanny-juvenile-kid population of the area, which forms a unit having little contact with other goat herds in surrounding areas. Observations to date indicate that interchange of individuals between herds is rare. The total herd has never been observed together at one time and is usually distributed throughout the area as solitary animals, family groups, and associations.

An important feature, as far as this study is concerned, is the almost complete lack of antagonism between members of an association, or between two adjacent associations. Outside the family group, no order of dominance has been observed other than a rather unobtrusive dominance of adults over kids. This does not imply that dominance may not emerge if the goats were subjected to different conditions. Aggressive behaviour was almost entirely limited to billies, but even these encounters were not vigorous. Of the five encounters observed between billies, none had any conclusive termination such as the driving away of the loser, and in all cases the billies grazed close together at the end of the encounter. There is no observation to suggest that the presence of billies in the association during the summer changes the organization, for there were still no signs of leadership.

Different strains of goats may have different behaviour patterns. For instance, a strict order of retreat with kids leading, followed by nannies and then billies was described for *Capra hircus aegagrus* by Darling (1957) but was not observed in this area. As there are at least two different varieties of domestic goat in New Zealand, it is important to distinguish the different ancestral stocks in any further behaviour studies.

INDIVIDUAL AND HERD HOME RANGE

Data gathered on the home ranges of fifteen nannies and kids in the area shows that there is a large area jointly occupied by all these goats. This range measures about six hundred yards by nine hundred yards on the sketch map (Figs 2–5). The actual distances are rather greater owing to the dissected nature of the country, the ridges of which rise five hundred to a thousand feet above the streams. The maximum distance across a nanny's home range was 1,225 yards (see Fig. 2). As described elsewhere in the paper, the boundary of the range is not a clearly defined line. However, such a high proportion of the observations on individually recognized goats was made within a circumscribed area (see Fig. 3) that the herd home range was arbitrarily defined as the area within which 90% of the observations were made.

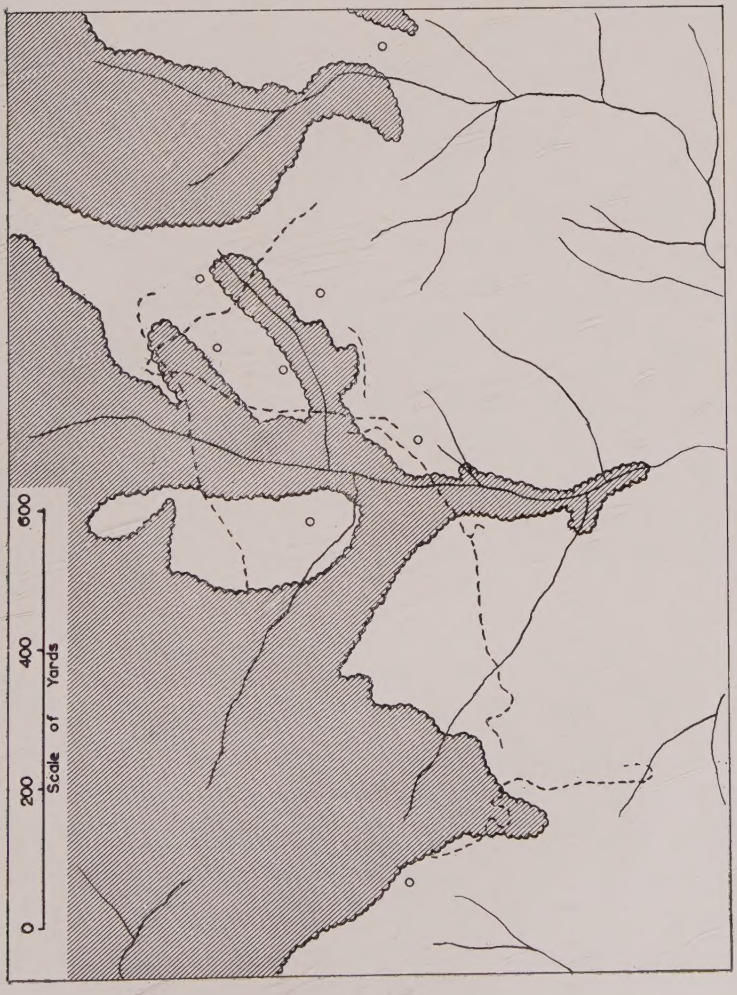


FIG. 2.—Sketch map: Broken lines indicate all observations throughout one year of N3, the adult female having the greatest home range of any nanny observed. Circles show her location when she was not travelling during the period of observation. Observation periods were usually more than three hours.

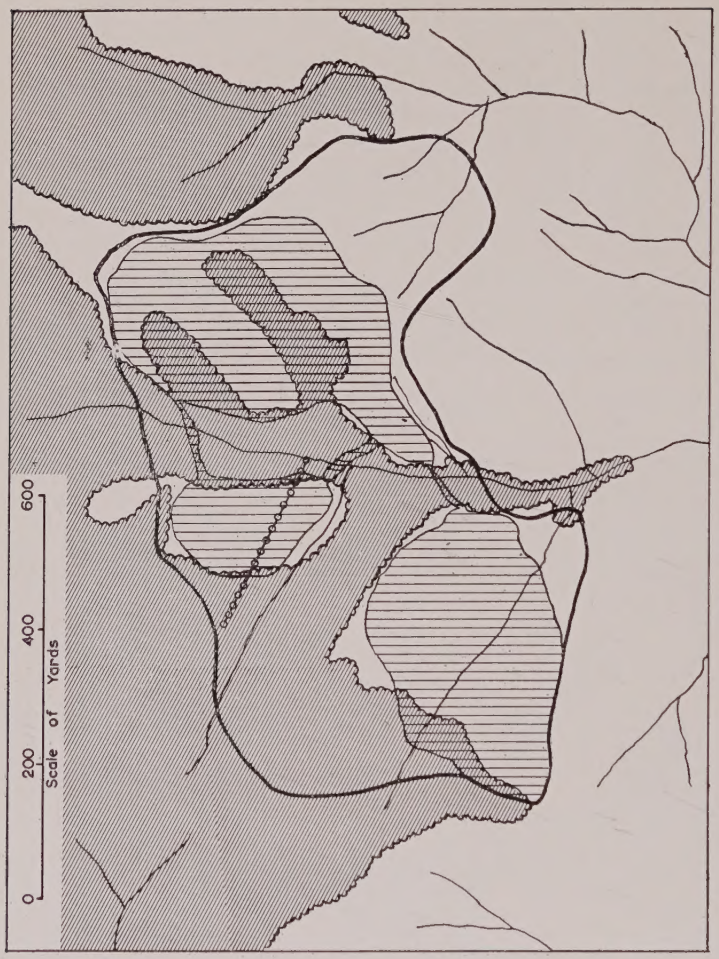


FIG. 3.—Showing that the pattern of use is this herd range consisted of three areas of higher use compared with the surrounding area. The location of a faeces count line is shown.

The greatest distance across this herd home range was 1,050 yards. Observed movements typical of a nanny and a juvenile are illustrated in Fig. 4. As the billies come on to the nanny range in the summer and have in addition a winter range of unknown size, the billies' yearly range is considerably greater.

The following observations suggest that billies do not necessarily use the same summer range each year: of the nine billies that appeared on the nanny range in the 1956–57 summer, only three returned in the 1957–58 summer, but five other new billies also came on to the range; and one billy that came on to the range in 1956–57 was seen next summer to be with another herd of nannies more than a mile away. These two herds apparently do not mix.

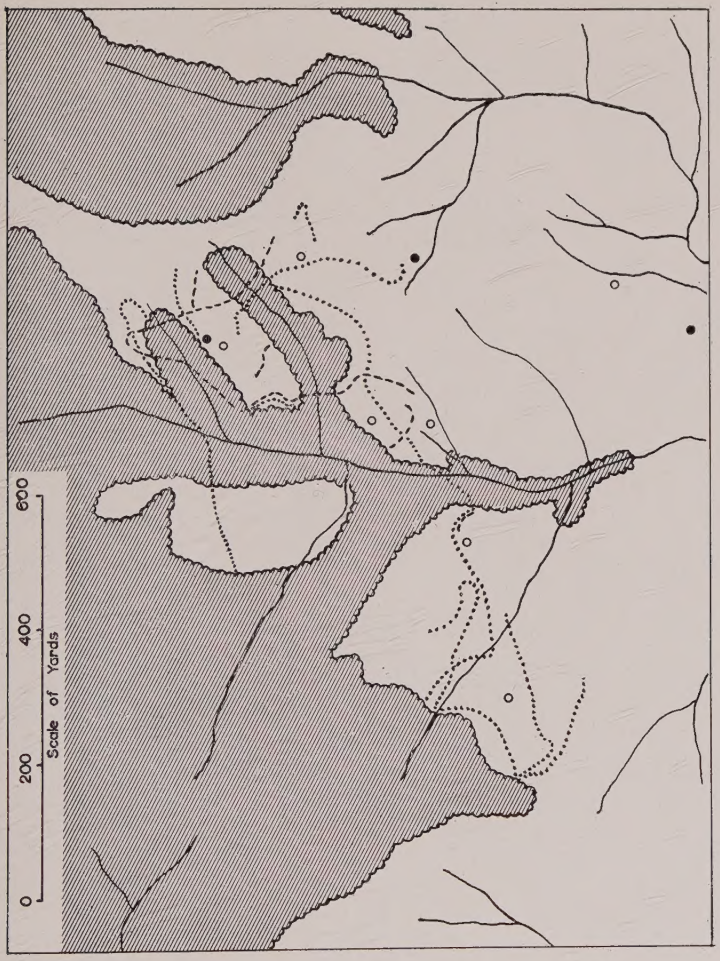


FIG. 4.—Broken lines indicate observed movements of a typical adult female (N4) and of a typical male juvenile (J3) throughout a period of one year. Circles show position of these goats when not travelling during the period of observation, which usually extended for a period of more than three hours.

Habitat Components of the Herd Home Range

Within the herd home range (Fig. 3) were three areas which sustained higher use than the surrounding area. The vegetation of each high-use area was predominantly either sheep pasture or native grass interspersed with low shrubs. These high-use areas, while having similar major components, differ in the ratio of shrubs to grass, from mostly grass but including bracken fern and shrubs, to mostly shrubs with grass in patches. One of these areas was unimproved sheep pasture cleared from the forest about fifty years ago, while another was a fire-induced clearing within the forest.

FIG. 5.—Showing the observed limits of occurrence of sheep and of goats in relation to major components of the habitat.

An aerial photograph taken in 1943 shows considerably less scrub than is now present. This indicates that the high-use areas are reverting to forest in the presence of grazing by goats and to a lesser extent by sheep. As this constitutes a gradual change in the habitat, it is possible that it will ultimately result in changes in the shape of the herd home range.

To test the possibility of overrating the open areas as high-use areas because of the ease with which the goats could be observed there, a forty-plot faeces count line was run through the forest and out on to the high-use area estimated to be least used by goats. Twenty plots were in the forest and twenty in the open. Intensity of animal use is expressed in terms of defecations per 100 plots. From the plots in the open area, 100 defecations per hundred plots were recorded, and in the forest twenty defecations per hundred plots were recorded (χ^2 7·84; P, ·01 to ·001), thus validating the term "high-use area".

The high-use areas are connected by a few well-used trails, the formation of the latter apparently relating to topography. Unlike the sheep trails that formed through all parts of the study area occupied by sheep, the main goat trails occurred only where there were very few accessible routes between high-use areas (Fig. 3). These occurred in steep country along a narrow ridge, where a route crossed a stream between two waterfalls, and where it was necessary to use a narrow route in skirting bluffs. Apparently if many possible routes are present, no definite trails develop as the goats are seldom seen using exactly the same route twice when not confined by topography to a single trail. These goats seldom travelled directly between two points, but tended to meander in their course.

The high-use areas seemed to serve the main feeding requirements of the herd as well as providing clear areas for fighting, mating, and sunning. Forest areas are less used, and are apparently utilized by this herd mainly for shelter, concealment from shooting, and for bedding at night. They are also used as alternative feeding areas in bad weather or when the goats are disturbed. Silver beech (*Nothofagus menziesii*) and kamahi (*Weinmannia racemosa*) constitute the main components of the canopy. In this area at least, interspersed grass and shrub areas, and forest areas are the two main components of the herd range.

Factors Influencing Range Boundaries

While it seems fairly clear that the size of the home range is influenced by the abundance, quality, and ratio of the habitat elements in the area, it is difficult to learn what influences the actual formation of the home-range boundary. The portion of the herd range that extended into the unforested country was most easily observed, and as individual and herd home range boundaries became increasingly familiar, a search was made for some of the factors governing boundary formation.

Early in the study it was seen that the upper limit of the sheep range approximately coincided with the lower limit of the goats' range. To test the theory that some form of antagonism between the two species was responsible, many observations of contacts between sheep and goats were made and their separate range boundaries accurately plotted (Fig. 5). Sheep have been seen to move quickly out of the path of a billy but resume grazing thirty seconds later. When a juvenile goat found a ewe in its path, however, it made a semi-circular detour while the sheep stood firm, stopped grazing, and stared at the goat. Sheep and goats have many times been seen to graze undisturbed within fifteen yards of one another. From these and similar observations, it is considered that there is not enough antagonism between the two species to influence the range boundary, especially as there is more than one observed area of overlap in their respective ranges.

Goats that have been hunted take alarm easily at the sound of shooting. For example, while a group of three goats was under observation at the forest margin six days after a shooting party had shot a goat in the area, a hunter commenced shooting in a valley more than a a mile away and two valleys distant. Although the forest muffled the

shots to some extent they were plainly audible as the hunter was using a heavy rifle which sounded like a ·303 calibre. Five rapid shots were fired. At the second shot the goats got to their feet and at the fourth they ran into the forest.

The possibility that the boundary might be directly influenced by shooting activities was considered and an effort was made to find out how often this area was hunted. During 1957 it is known to have been hunted at least four times, but for only a day or possibly two on each occasion. None of these hunts was very intensive and during the year only four goats are known to have been shot. Hunting probably causes a temporary reduction in the distance covered by goats in a day, as they will not venture far from the forest for several days after shooting has taken place. Although shooting had a temporary influence on activity, it was apparently not intensive enough by itself to permanently influence the boundary of the herd's range.

Since all the habitat components necessary for the goats' existence are found within the home range, it seemed logical to look for some relation between the habitat and the home-range boundary. There was no clearly defined habitat change closely corresponding to the range boundary, as was the case with the sheep. The range boundary of the study herd did, however, appear to be loosely related to one of the habitat components—cover. Where there were medium-density scrub gullies, the lower boundary of the goat range extended farther away from the forest, but kept close to the forest where the gullies were free from cover. There was no evidence of the boundary being a clearly defined line: it was more in the nature of a band or zone.

These observations raise further questions; for example, if one habitat component, cover, can influence the home-range boundary in one area, the spacing of the other components, shrubs for example, may result in a similar response in other areas where there is unlimited cover, but where shrubs palatable to goats are limited. Could frequency and intensity of hunting in an area modify the distance goats are observed from cover?

When the billies came down from the forest in the summer, they were disposed to wander more than the nannies. As an association of goats will follow the purposeful movement of any of its adult members, the billies' presence temporarily influences the movements of the rest of the herd. This may be explained to some extent by the experiments of Scott and Stewart (1946), who reported a lack of correlation between leadership and dominance in a flock of eighteen goats where order of leaving an area was not correlated with order of success in excluding other goats from food. Although the maturing males eventually move out of the nanny-kid range, this movement does not seem to extend the herd range, and juvenile females remain within the boundaries of the parent herd's range. The billies tend to have a range covering at least two nanny herds, which contributes to a reduction of inbreeding and facilitates an exchange of genes between isolated nanny herds. This idea is illustrated by Fig. 6. Nanny herds A, B, and C contribute males to the ABC billy herd, and these males may breed with any herd. There is apparently only very limited exchange between the nanny herds, as mentioned before, but it does occur.

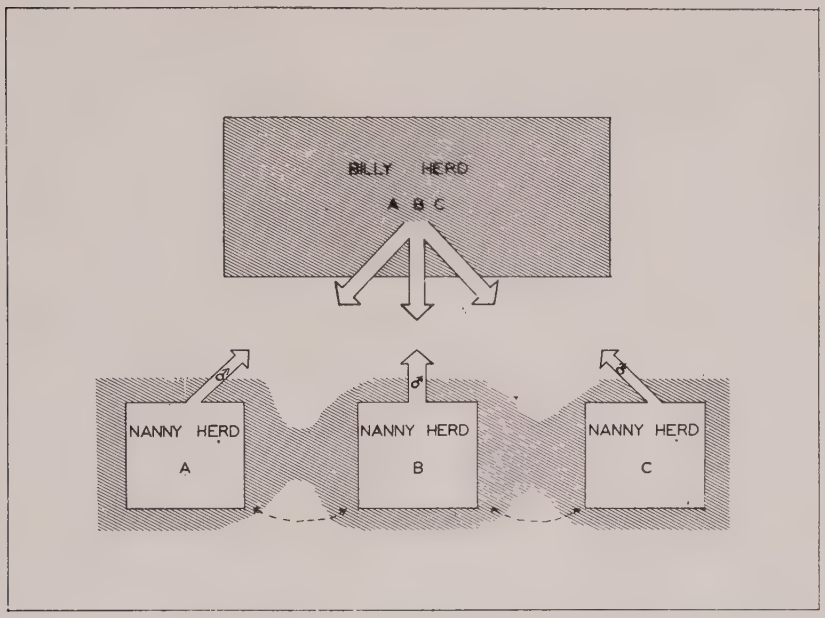


FIG. 6.—Model constructed to show relation between billy and nanny-kid herds. Young males move from three nanny-kid herds (A, B, and C) to a common billy herd (ABC). Shaded areas around nanny-kid herds represent the ABC billy herd's summer range, which includes the yearly ranges of the three nanny herds.

DISCUSSION

Importance has been attached to the shape of the home range by Dice (1952) who suggested that variations in the shape and in the size of the home range were closely related to differences in the distribution of the various requirements for the animals' existence. These generalizations are consistent with everything observed in the present study, and, in addition, it is suggested that there are areas within the used portion of the home range that are not used at all. For some species, the home range must take into account not only the variations due to seasonal changes but also sexual differences with respect both to the size of the living area and to the association of each sex with different habitat elements. In short, what is attempted here is a preliminary description of the pattern of use that has developed within a small-herd range of goats.

From the point of view of understanding the distribution of feral goats in an area that includes many herds (for example, the entire

mountain range on which this study population occurs), one logical extension of the present study would be to study the distribution of these apparently separate herds.

Management

Since the nanny-kid herd forms the most clearly defined unit of the total populations not only of the study area but also of similar adjacent areas, it would be appropriate to adopt the nanny-kid herd as the unit of management. If the conservation requirements of the country over which the goats range clearly call for a reduction in the intensity of goat browsing and grazing, then the nanny-kid herds would be more suitable for control techniques than the billy herds. In this area the billies spend much more time in the forest than do the nannies, and for this reason it would be more difficult to reduce their numbers. The nanny-kid herds are much more accessible, to a considerable extent more localized, and are the actively reproducing portion of the population. It is possible that three-quarters of the billy population could be killed without reducing the kid crop of the next season, as one billy can fertilize several nannies.

Over the past eight years, sporadic shooting has been unsuccessful in reducing the numbers of animals in this area or in dispersing the goats (L. Battersby, pers. comm.) although it has made them more wary. It is clear that the practical problem of control consists of dealing with herd after herd on their individual home ranges. Recording the total number of goats taken from the drainage would not in itself be indicative of the extent to which operations were effective; for example, the total numbers may include males, may be only a small fraction of the nanny-kid herd, or may represent the elimination of some nanny-kid herds while not touching others. The effectiveness of control activities on the goat population should be measured by the proportion of each nanny-kid herd eliminated by these activities.

Other herds in the vicinity of the study area appeared to differ not only in numbers but also in the pattern of use they make of the area in which they live. It is therefore essential to consider each herd together with its herd range as a separate entity with characteristics peculiar to itself, and detailed management techniques appropriate to one herd are not necessarily appropriate to another herd near by. This may be a practical point to keep in mind both for control activities and for research, at least until enough data are forthcoming from future studies of other herds to permit broader generalizations.

Since shooting with powerful rifles such as the ·303 calibre causes the goats to become excessively wary, it is evident that the use of this type of rifle, for all its advantages of range and power, is not ideally suited for the control of goats. Consequently, a more appropriate method worth trying is the use of a low-power rifle with a silencer so that the disturbance of the rest of the herd can be kept to a minimum. Such

a method has been used by both writers on goats outside the study area with such success that it is considered that it would be worth while to test hunting techniques based on this weapon in the hands of a specially trained team of hunters for comparison with techniques now in use by goat shooters. It is important that any action to reduce or eliminate a herd should be carried out quickly and quietly to reduce disturbance of the unshot remainder of the herd. No matter how experienced the shooter assigned to reduce the goats in this area, it could not be expected that a high proportion of the nanny-kid herd could be eliminated by the normal hunting method of walking along ridges, slopes, and creek beds until animals are encountered. By this method, several animals are usually shot, thus greatly increasing the wariness of the remaining goats which on subsequent days become so difficult to stalk that the shooting effort is usually re-distributed to other undisturbed areas where the process is repeated.

Winter, when the herds are most localized and when the billies are not present to cause a temporary expansion of the nanny-kid herd range, is suggested as the best time of the year to apply control techniques in the area.

The pattern of use within the area would also be important to consider when planning poisoning operations. Poisoning would probably be more difficult to apply in this area, for even the task of locating and baiting the high-use areas in the nanny-kid home range would involve more time and expense and a higher degree of skill and training on the part of the field team than would locating the nanny-kid areas and systematically shooting them.

It is axiomatic that the distribution and abundance of animals are closely associated with their environment. One of the four components of an animal's environment as described by Andrewartha and Birch (1954) is "a place in which to live" or, as used in this report, the "habitat". The importance of the habitat as a factor influencing animal numbers in New Zealand has already been suggested for rabbits (Howard, 1958) and for deer (Riney, 1956). An example of the practical application of this principle to the present study is that an increase in numbers can be brought about by altering the habitat to one more favourable to goats. This could be done in this area by burning off some of the scrub (*Cassinia* sp.) which is not used as browse by the goats. As shown in Fig. 5, dense areas of scrub are not favoured, and, as this scrub is increasing, the habitat is at present becoming less favourable. It is a common farming technique here periodically to burn the scrub to create additional sheep pasture, and these fires incidentally create a more favourable habitat for the goats along the margin of the forest.

An increase or decrease in the numbers of sheep in adjacent areas would probably have little effect on goat numbers, as the ranges of these two species do not overlap to the extent that there is active competition for available food.

Acknowledgements

The writers would like to thank Mr L. Battersby for initially suggesting this area for study and for the use of his hut; Mr Burrell and Mr McCarthy for permission to operate on their property; Mr P. Dwyer and Mr J. S. Watson for making valuable suggestions; and Miss Ann Darrall for help at all stages of the work.

References

Andrewartha, H. G.; Birch, L. C., 1954: "The Distribution and Abundance of Animals". University of Chicago Press: 782 pp.

Amschler, J. W., 1929: Zur Revision der Rassen—und Abstummungsfrage der Hausziege. *Zuchtungskunde 4 (10)*: 465–68.

Darling, F. Fraser, 1937: Habits of Wild Goats. *J. Anim. Ecol. 6 (1)*: 21–2.

Dice, L. R., 1952: "Natural Communities". Ann Arbor, University of Michigan Press. 321 pp.

Howard, W. E., 1958: The Rabbit Problem in New Zealand. *N.Z. Dep. sci. industr. Res. Inf. Ser.* 16: 47 pp.

Riney, T., 1956: Comparison of Occurrence of Introduced Animals with Critical Conservation Areas to Determine Priorities for Control. *N.Z. J. Sci. Tech. B 38 (1)*: 1–18.

———, 1957: The Use of Faeces Counts in Studies of Several Free-ranging Mammals in New Zealand. *N.Z. J. Sci. Tech. B, 38 (6)*: 507–32.

Scott, J. P.; Stewart, J. C., 1946: Lack of Correlation between Leadership and Dominance in a Flock of Goats *Anat. Rec. 96 (4)*: 552–53.

BIOLOGICAL AND CHEMICAL CHANGES FOLLOWING SCRUB BURNING ON A NEW ZEALAND HILL SOIL:

2—CHANGES IN SOIL pH

By R. B. Miller and M. FitzPatrick, Soil Bureau, Department of Scientific and Industrial Research, Wellington

(Received for publication, 2 March 1959)

Summary

Regular pH determinations have been made for a year on a burnt-over area on the Taita Experimental Station. For comparison, soil pH's on adjacent unburnt areas were also measured. In all, over 1600 determinations were made. The high pH's found in the upper topsoil after burning were found to decrease to values near neutral in 8 to 10 weeks, and from then on to fall more slowly. The natural soil variability had to be considered and there were sufficient data for it to be measured and for some conclusions about sampling methods to be drawn. The changes in pH and salt effect have been correlated with pasture establishment in the first year after burning.

Introduction

In a recent study of the effects on soil of scrub burning (Miller, Stout, and Lee, 1955), it was noted that the soil pH increased markedly after burning and then fell over a period of 10 months to a value little above normal. The measurements, however, were made at relatively long intervals, there were no unburnt controls and only the top inch of soil was sampled. The rate of change of pH was therefore not established accurately and the effects on the deeper soil layers were not considered. Furthermore, as only composite samples were taken, no measure of the natural variability of the soil pH was obtained. It was therefore decided, when another area was burnt, to investigate these factors more closely.

Experimental Site

The burn on this occasion was on a firebreak to the east of the Taita Experimental Station buildings. A break of 20 yards was cut in August 1954, in the mixed scrub vegetation of 10 ft to 12 ft high manuka (*Leptospermum scoparium*) with some gorse (*Ulex europaeus*), kamahi (*Weinmannia racemosa*), and occasional pines (*Pinus radiata*), all up to 35 years old (Druce, 1957). The cut scrub was built into heaps so that the burning could be better controlled and burnt on 21 September 1954. Good burns were obtained, all the scrub being destroyed, including the wood.

One of the heaps which had not been disturbed after burning and which had not been sprayed down with the fire hoses was selected and marked off.

The typical Taita silt loam profile found over most of the area of this slope is:

A_0 { L 1 in undecomposed dry litter of manuka and gore,
F 1 in partially decomposed moist litter,

A_1 4 in dark greyish brown (10YR 4/2) silt loam,

B 4 in yellowish brown (10YR 5/6) silty clay loam,

C 16 in yellowish brown (10YR 5/8) clay loam, on weathering greywacke.

The profile varies with slope, on steeper slopes it is more shallow, the topsoil is thinner and weathering rock is found at about 12 inches depth. The site is moderately steep with a north-westerly aspect, the angle of slope varying from 21° to 26°.

SAMPLING AND METHODS

On each sampling date samples were collected from the sites shown in Fig. 1, i.e., two from under standing scrub, two from the cleared, but unburnt, area, two from the lightly burned fire edges, and one from the heavily burned centre of the fire. The first samples were taken on 22 September 1954, and then further sets were taken at weekly intervals for 12 weeks, at 2- to 3-weekly intervals for another 12 weeks, and then at 2-monthly intervals till September 1955. Twenty-one sets were taken in all. Each site was sampled at six depths as follows:

A dry, undecomposed top-litter

B moist, partially decomposed under-litter

C 0 to $\frac{1}{2}$ in of mineral soil

D $\frac{1}{2}$ to $1\frac{1}{2}$ in

E $1\frac{1}{2}$ to $2\frac{1}{2}$ in

F 5 to 6 in

The samples were collected by spade from areas about 6 in square, 100g to 200g of soil being taken for each sample. In sites 3, 4, and 5, the litter layers were partially destroyed by the fire in some parts and wholly destroyed in others. In these places surface scrapings of ash and partially burnt litter were collected.

The pH determinations were made in water and N KCl solution, with soil to solution ratios of $1:2\frac{1}{2}$ for the mineral soils and 1:5 for the litters. The samples were not dried, but weighed out as soon as possible

after sampling. The solution was added and the suspension stirred and stood overnight. The determinations were made at 20° C using a glass electrode with a Cambridge portable type pH meter. The results were readily reproducible and little drift was encountered.

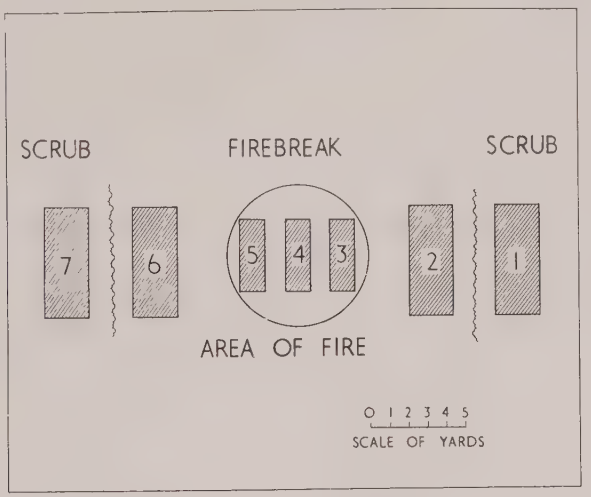


FIG. 1.—The area of the fire shown in relation to the firebreak with sampling sites shaded.

RESULTS

As pH is a logarithmic function of the hydrogen-ion concentration, to get a true mean pH value each pH should be converted to a hydrogen-ion concentration, the average taken, and this re-calculated back to pH. The true mean of pH4 and pH5 thus comes to 4·26, not 4·5. However, when the variation between the samples is small the arithmetic mean of the pH values is sufficiently accurate, particularly as here the main concern is with trends.

Table 1 contains arithmetic means for all the samples collected. To simplify the general picture the 21 samplings were first grouped into three groups of seven, group I containing the samples taken between 22/9/54 and 5/11/54, group II those taken between 12/11/54 and 6/1/55, and group III those between 21/1/55 and 27/9/55. Then samples from like sites 1 and 7, 2 and 6, and 3 and 5 were grouped.

The results show clear downward trends in the two top horizons of the fire sites 4, 3, and 5. There is also a slight fall in 2 and 6. The other topsoils and all the D, E, and F samples vary little over the three periods.

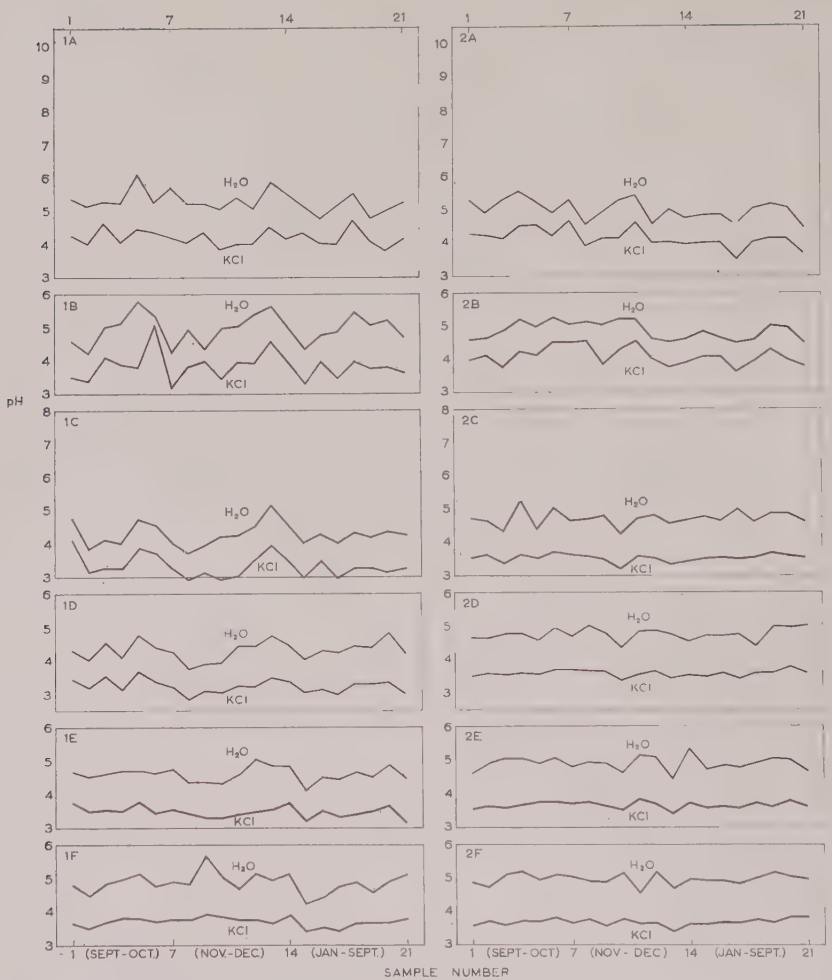


FIG. 2.—The pH_{H_2O} and pH_{KCl} values for sites 1, 2, 3, and 4 on the 21 sampling dates.

Figure 2 shows the actual pH values obtained over the period for some of the samples. They show the trends mentioned quite clearly. They also provide data for consideration of variability factors. Figure 3 shows the difference between pH_{H_2O} and pH_{KCl} for a burnt (4) and an unburnt site (1).

DISCUSSION OF RESULTS

Before considering the changes taking place as a result of burning, the natural variability of the soil must be considered to see if it affects the

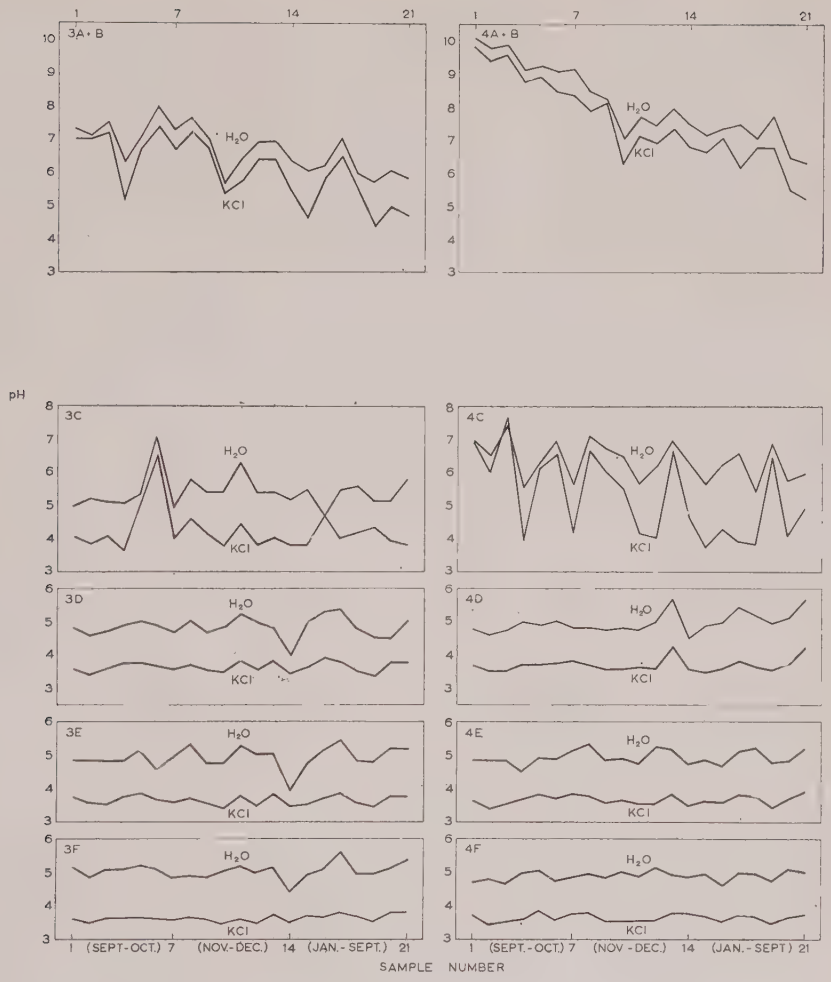


FIG. 2.—*Continued.*

conclusions drawn. Most investigations on the subject, for example those of Raupach (1951), have shown relatively large variations, even within small areas.

NATURAL VARIABILITY

A study of the results from unburnt sites 1, 2, 6, and 7 given in the tables and figures shows:

(a) The samples taken at various times vary in pH appreciably from site to site and within the same site. The variability of pH_{H_2O} is greater than that of pH_{KCl}.

(b) The variability in both pH_{H_2O} and pH_{KCl} decreases with depth and is greater in sites 1 and 7 (under scrub) than in 2 and 6 (cleared).

(c) The variation in Δ pH ($pH_{H_2O} - pH_{KCl}$) corresponds closely with that of pH_{H_2O}. There is no such correspondence of pH_{KCl} with Δ pH.

TABLE 1.—Mean pH Values for all Samples for the Four Types of Site, Grouped into Three Periods.

Samples	pH_{KCl} Group I	pH_{KCl} Group II	pH_{KCl} Group III	pH_{H_2O} Group I	pH_{H_2O} Group II	pH_{H_2O} Group III
1 and 7 (standing scrub)						
A	4·5	4·4	4·6	5·6	5·4	5·5
B	4·4	4·4	4·2	5·4	5·4	5·2
C 0 to ½ in	3·7	3·5	3·5	4·8	4·7	4·8
D ½ to 1½ in	3·5	3·4	3·4	4·7	4·5	4·7
E 1½ to 2½ in	3·6	3·5	3·5	4·9	4·6	4·8
F 5 to 6 in	3·6	3·7	3·6	4·9	4·9	4·8
2 and 6 (cleared, but not burnt)						
A	4·3	4·1	4·0	5·2	5·0	4·8
B	4·2	4·0	4·0	5·1	5·1	5·0
C	3·5	3·5	3·6	4·7	4·7	4·8
D	3·6	3·5	3·6	4·7	4·8	4·8
E	3·6	3·6	3·6	4·8	4·9	4·8
F	3·6	3·5	3·6	4·9	4·9	4·9
3 and 5 (edge of fire)						
AB	6·9	6·4	5·3	7·3	6·9	6·2
C	4·2	4·0	3·9	5·3	5·4	5·2
D	3·6	3·6	3·6	4·8	4·8	4·9
E	3·6	3·6	3·6	4·8	4·8	5·0
F	3·6	3·6	3·6	4·9	4·9	5·0
4 (centre of fire)						
AB	9·1	7·2	6·3	9·5	7·7	7·1
C	5·9	5·4	4·4	6·5	6·5	6·1
D	3·7	3·7	3·7	4·8	4·9	5·2
E	3·7	3·6	3·7	4·9	5·0	5·0
F	3·7	3·7	3·7	4·9	5·0	4·9

The lack of seasonal trends and the lack of correspondence in the pattern of changes down the profiles suggest that the causes of variation here are within the soil. The correspondence between Δ pH and

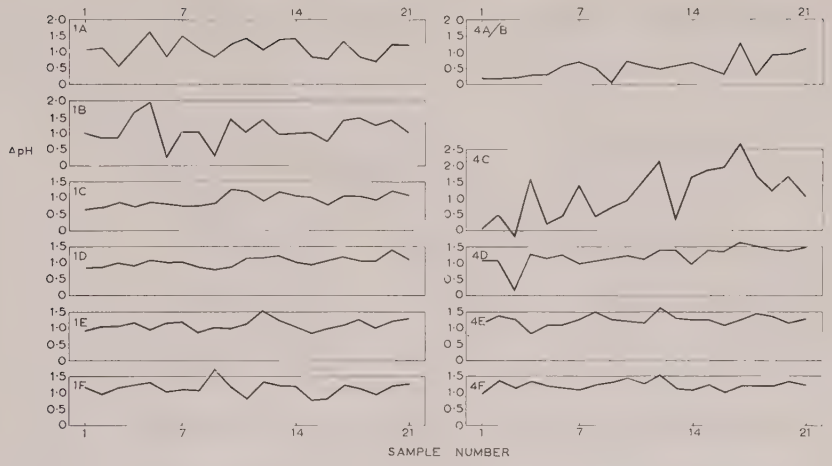


FIG. 3.—The ΔpH ($pH_{H_2O} - pH_{KCl}$) values for sites 1 and 4.

pH_{H_2O} and its independence of pH_{KCl} points to salt as one of the varying factors. The pH_{H_2O} is very sensitive to changes in salt level and this is one of the reasons why measurements in N KCl or 0·01 N $CaCl_2$ are often preferred.

The other factors could not be isolated from these results but must depend on small differences in such things as soil parent material, drainage, present or past vegetation patterns, and possibly uneven ash deposits from previous burns. These natural differences are usually less than a pH unit. However, when the salt effects are superimposed on the soil effects as in pH_{H_2O} determinations, differences of over a pH unit are common, even within areas of only a few square yards.

Statistical analyses of the results from the A, C, and F samples of sites 1 and 2 (Table 2) give an estimate of the extent of variability. They show, for instance, that the pH_{H_2O} of approximately a third of the A samples lie outside the range 4·8 to 5·5 and a third of the F samples outside the range 4·6 to 5·1. To get a set of mean pH_{H_2O} values for the profile, accurate to 0·1 pH units, composite samples with at least 14 subsamples would have to be taken. For pH_{KCl} the variability is smaller, but still considerable.

TABLE 2.—Results of Statistical Analysis of Sets of 42 pH Values from A. C, and F Samples, Sites 1 and 2.

Depth (in)		Mean	Range	Standard Deviation	Standard Error of the Mean	No. of samples for Standard Error 0·10
			pH_{H_2O}			
Dry top litter	1, 2 A	5·16	4·48-6·07	0·33	0·051	10
0-½	1, 2 C	4·50	3·70-5·31	0·37	0·057	14
5-6	1, 2 F	4·87	4·20-5·66	0·25	0·039	7
			pH_{KCl}			
Dry top litter	1, 2 A	4·16	3·52-4·73	0·26	0·040	7
0-½	1, 2 C	3·38	2·90-4·08	0·28	0·043	8
5-6	1, 2 F	3·68	3·40-3·88	0·11	0·017	2

The natural variability will not greatly affect the broad changes taking place as a result of burning. It is, however, large enough to make single samples a very unreliable index of the soil pH. To illustrate this some of the pH_{H_2O} values for individual profiles from unburnt sites are shown in Table 3 with the mean value for 84 profiles.

TABLE 3—.pH_{H_2O} Values for Some Individual Profiles Compared with the Mean Value.

Level	Horizon and Depth	Mean	a	b	c	d	e
A B	A_0 (litter)	5·22	5·0	4·7	6·0	4·6	4·8
C D E	A_1 (0-2½ in)	4·75	5·0	5·0	4·9	4·9	4·1
F	B_1 (5-6 in)	4·87	5·0	5·1	4·6	4·8	5·7

In the mean the pH falls from the A_0 to the A_1 horizons and then rises slightly in the B_1 horizon. In (a) the pH is uniform down and profile, in (b) it rises and in (c) it falls. In (d) it rises, then falls and in (e) it falls to 4·1 and then rises to 5·7. Any one of these, if sampled singly in this way, would give a false impression of the mean soil pH. In practice when single samples are taken each sample normally covers a greater depth range—often 4 to 6 in.—and a greater quantity

of soil—2 lb or more—is taken. This procedure tends to smooth out differences to some extent although the area sampled is often little more than in this investigation. To get a reliable mean value it is necessary to take a number of sub-samples. Sixty one-inch cores as used at another site at Taita (Miller, *et al.*, 1955), or 15 larger samples, similar to those taken in this investigation, would be adequate.

THE INFLUENCE OF BURNING

The factors of natural variability are present in all the sets of results, but the main effects of burning come out clearly. In the previous study the pH in the litter rose about 2 units after the fire, and then fell one unit in 2 months and a further $\frac{1}{2}$ unit in the next 8 months. Here the general effects are similar but the larger number of samples allows the trends to be studied in more detail. In Fig. 2 a slight trend is evident in both sets of pH results in 2A, and there are clear trends in 3A/B, 4A/B, and 4C. In 2A an analysis of variance on the 3 chronological groups of 7 pH_{KCl} values, showed significant differences at the 5% level. The analysis was done on hydrogen-ion concentrations calculated from the pH. The trend evident in 2A is also apparent in 6A and is an indication of the changes occurring in the litter when the scrub under which it was formed is cleared. It is not related to burning and, as burning destroyed most of the litter, would not be a contributing factor to the trends in the burnt plots.

The pH values for the surface layers of the burnt area fall from very high values found immediately after the fire to values not greatly above normal. In 4A/B the pH_{H_2O} was above 9 for six weeks, between 8 and 9 for two weeks, and then between 7 and 8 for eight months. In 3A/B the values were mainly between 7 and 8 for the first ten weeks, and after that mainly between 6 and 7. The pattern, therefore, is a rapid initial fall followed by a much slower one that is still going on after a year. The cause of the changes is the deposition of highly alkaline ash during burning. Ash samples in water usually gave pH values of over 12. Over the weeks following the fire the alkalis are neutralized, the salts are leached from the soil and the pH falls. A heavy ash deposit will, however, raise the base status of the soil considerably so that it might be years before the pH falls to its original level.

The reduction in salt concentration by leaching or run-off can be followed in the changes in ΔpH in Fig. 3. Because of the large pH range in site 4 these differences do not appear nearly as great as they are in fact. In Table 4 they are compared with hydrogen-ion concentration differences ($\Delta[H^+]$. It can be seen that the differences in the F horizons of the seven sites are relatively small, but in the A horizons they are very great. In the burnt sites, 3, 4, and 5, $\Delta[H^+]$ is negligible.

Over the year $\Delta[H^+]$ increases again and at the end is similar to that of the unburnt soils, showing that the salt influence has largely disappeared.

TABLE 4.—Differences in pH as Determined in Water and KCl, Expressed as ($pH_{H_2O} - pH_{KCl}$) or ΔpH, and as Differences in Hydrogen-ion Concentration $\Delta[H^+]$, in A and F Samples from Sites 1 to 7, Taken on the First Sampling Date.

	A and AB samples			F samples		
Site	pH_{KCl}	ΔpH	$\Delta[H^+]$	pH_{KCl}	ΔpH	$\Delta[H^+]$
1	4·27	1·08	$4{\cdot}9 \times 10^{-5}$	3·62	1·16	$2{\cdot}2 \times 10^{-4}$
2	4·25	1·06	$5{\cdot}1 \times 10^{-5}$	3·59	1·22	$2{\cdot}4 \times 10^{-4}$
3	7·02	0·28	$4{\cdot}5 \times 10^{-8}$	3·62	1·48	$2{\cdot}3 \times 10^{-4}$
4	9·88	0·20	$4{\cdot}9 \times 10^{-11}$	3·75	0·99	$1{\cdot}6 \times 10^{-4}$
5	9·61	0·09	$4{\cdot}6 \times 10^{-11}$	3·49	0·94	$2{\cdot}9 \times 10^{-4}$
6	4·20	0·99	$5{\cdot}7 \times 10^{-5}$	3·41	1·36	$3{\cdot}7 \times 10^{-4}$
7	4·82	1·15	$1{\cdot}4 \times 10^{-5}$	3·51	1·55	$3{\cdot}0 \times 10^{-4}$

EFFECTS ON PLANT GROWTH

When soil samples were taken, notes were made on the plant growth. Three days after the burn the area was sown with a grass-clover mixture and then, in May 1955, it was oversown with the same species. The firebreak, with the exception of the sampling area, was fertilized with 5 cwt of lime and 3 cwt of molybdenized superphosphate per acre in March 1955.

The first plants to appear were gorse which, after 5 weeks, was thick in parts of the edges of the burnt area and beginning to appear in the centre. After 8 weeks gorse was well spread over the whole area, bracken (*Pteridium aquilinum* var. *esculentum*) was also growing rapidly everywhere and occasional clumps of clover were noted. In the following few weeks grass came through in all parts and clover spread slowly. Through the summer there was little development except in moist hollows, but in the autumn both grass and clover came away vigorously. In the spring (September 1955), however, the growth of both grass and clover was very poor. The adjacent fertilized areas which up till this time had not differed from the sampling area, developed a close and vigorous pasture cover of grasses and clovers.

It may be concluded that the high pH and salt content of the soil in the first 8 weeks after burning restricted the germination and growth of pasture plants. From then for about a year the fertilizing effect of the ash was sufficient to maintain good growth. After a year the pasture deteriorated rapidly due to the lack of phosphate and molybdenum.

ACKNOWLEDGEMENT

The authors wish to thank Mr H. S. Roberts of the Applied Mathematics Laboratory, D.S.I.R., for the analysis of variance of the 2A samples and for helpful discussion on other statistical methods.

REFERENCES

DRUCE, A. P., 1957: Botanical Survey of an Experimental Catchment, Taita, New Zealand. *N.Z. Dep. sci. industr. Res. Bull.* 124.

MILLER, R. B.; STOUT, J. D; LEE, K. E., 1955: Biological and Chemical Changes following Scrub Burning on a New Zealand Soil. *N.Z. J. Sci. Tech. B37* : 290-313.

RAUPACH, M., 1951: Studies in the Variation of Soil Reaction. *Aust. J. agric. Res. 2* : 73-91.

THE AIR POLLUTION PROBLEM IN CHRISTCHURCH, NEW ZEALAND

By L. WILKINSON, Dominion Laboratory, Department of Scientific and Industrial Research, Christchurch

(Received for publication, 5 January 1959)

Summary

A short description is given of the factors which influence air pollution in Christchurch. These factors include climate, topography, and consumption of solid and liquid fuels. A limited survey has been made of the incidence of smoke, grit, dust, and sulphur dioxide in the city atmosphere. Comparisons have been made with conditions in London and Los Angeles.

The survey shows that, while the problem at present is not as serious as in other countries, there is sufficient pollution of the Christchurch atmosphere in winter to warrant consideration of abatement measures. It is considered that measures adopted for the abatement of smoke in England should be applicable to Christchurch.

INTRODUCTION

In Canterbury, the first recorded observations on atmospheric pollution were made by Gray (1910), who measured the dissolved matter contained in rainwater collected at Lincoln, 14 miles from Christchurch.

During the early thirties, the late Dr C. Coleridge Farr, in association with Mr C. J. Banwell and on behalf of the Christchurch Sunlight League, made measurements on the precipitation of solid matter. Notes of these measurements are now held by the Christchurch Regional Planning Authority (pers. comm.).

In June 1954, the Dominion Laboratory commenced a systematic though limited survey of the incidence of sulphur dioxide in central Christchurch. In August 1956, observations were extended to include three suburbs, and, as opportunity permitted, measurements were also made of deposited matter and smoke.

Air pollution occurring in the southern area of Auckland, the largest city in New Zealand, has been described in the reports of a Commission of Inquiry (1955), of Damon (1957), and of Sullivan (1957).

The Health Act, 1956, and the Air Pollution Regulations, 1957, provide legislative authority to control emissions from industrial plants.

DESCRIPTIVE

Topography and Climate

Christchurch, latitude 45° S, is situated on the low-lying Canterbury Plains of the South Island. The centre of the city is 5 miles from the coast on the east and 2½ miles from the hills (2,000 to 3,000 ft) of Banks Peninsula on the south. Approximately 50 miles to the north and west are the foothills of the great mountain barrier of the Southern Alps (3,000 to 12,000 ft) which lie close to the western coast.

According to the New Zealand Official Year Book (Dep. Statistics, 1958), the mean daily temperatures over a period of many years range from 52·7° to 70·2° F for January, and from 34·7° to 50° F for July. The average annual rainfall is 26 inches, and the average number of rain days is 125 per annum.

Calm days occur more frequently in winter than in summer. Although the prevailing wind inland is the warm, dry, nor'-wester or "Fohn" wind, at the coast line colder north-easterly and easterly sea breezes predominate.

These conditions of topography and climate produce temperature inversions which prevent extensive vertical dissipation of pollutants. The effect of a temperature inversion is most evident during winter, when, in calm, frosty weather, visibility in the morning, late afternoon, or night is often greatly reduced by haze or low-level fog while the hill suburbs are in bright sunshine or moonlight. On a few occasions only, as shown in Table 1, fog may persist continuously for several days.

TABLE 1.—Dates and Duration of Persistent Fog Occurring in the 30-Year Period ended December 1957. (J. W. Beagley, A. L. Cullington, pers. comm.)

Year	Month	Dates of days with fog	Approximate hours of persistent fog
1933	June	26, 27, 28	56
1935	August	13, 14, 15	40
1939	April	11, 12, 13, 14, 15	84
1941	July	23, 24, 25	44
1949	June–July	28, 29, 30, 1	81
1952	July	16, 17, 18	44

The importance of temperature inversions on the incidence of air pollution has been stressed in publications describing the Los Angeles "smog" (Stanford Research Institute, 1954) and the London fog of December 1952 (Ministry of Health, 1954). In Los Angeles, temperature inversions are stated to occur on some 250 days each year.

Emission of Polluting Substances

Although, like Auckland (Sullivan, 1957), Christchurch is situated close to an extensive, shallow estuary, there is no evidence at the present time that the mud-flats and decaying vegetation in the Christchurch estuary make any significant contribution to the pollution of the city atmosphere. Complaints of odours arising from the estuary are confined to residents in the immediate vicinity, and there is no record of excessive blackening of paint similar to that which occurs periodically in areas around the Mangere Inlet, Auckland.

The Beaver reports (Committee on Air Pollution, 1953, 1954) indicate that the greatest single factor contributing to air pollution in England is the combustion of solid and liquid fuels. This factor is also true for Los Angeles, but, unlike England, no coal is burnt in Los Angeles, and gaseous emissions result largely from the combustion and handling of motor fuels and also from the burning of household wastes in back yards and incinerators. Christchurch is very dependent on coal and fuel oils as a major source of power and heat, despite the increasing and extensive use of hydro-electricity for these purposes.

Table 2 shows the major classes and amounts of materials burnt in New Zealand, Great Britain, and Los Angeles County.

The total amount of material burnt per head of population was 1·7 tons for New Zealand in 1955, 3·9 tons for Great Britain in 1953, and 3·7 tons for Los Angeles County in 1953.

The Christchurch Regional Planning Authority (Miss N. Northcroft, pers. comm.) estimates the population and area of the major built-up area comprising Christchurch as 181,000 and 35 square miles respectively. Steinberg (1958) gives the population and area as 8,270,000 and 722 square miles respectively for London, and 2,105,000 and 452 square miles respectively for Los Angeles City. The estimated amount of material burnt annually per square mile is therefore 8,800 tons for Greater Christchurch, 45,000 tons for Greater London, and 17,000 tons for Los Angeles City.

MEASUREMENT OF AIR POLLUTION

Description of Sites and Instruments

Observations in the Christchurch city area were made from the roof (90 ft above mean sea-level, and 70 ft above ground) of the Government Buildings situated at the south-eastern corner of Cathedral Square and Worcester Street. This site is in the centre of the commercial district. Gasworks and railway yards lie $\frac{5}{8}$ mile to the south. The major industrial areas are situated south-east ($2\frac{1}{2}$ miles), south ($\frac{1}{2}$ mile), and west ($1\frac{1}{2}$ miles).

Two cowl-covered "lead peroxide" instruments of the same design as those used in Great Britain for measuring atmospheric sulphur dioxide were put into operation in June 1954. The instruments were placed on the south-west and north-east corners of the building and are 23 yards and 50 yards respectively from the smokestack of two

TABLE 2.—Estimated Quantities (in British Tons) and Proportions of Various Materials Burnt in One Year.

Class of material	Quantity consumed			Proportion consumed		
	New Zealand (a)	Great Britain (b)	Los Angeles (c)	New Zealand	Great Britain	Los Angeles
	Million tons			Per cent.		
Coal:						
Domestic	0·52	36·8		14	19	
Electricity works ...	small	36·7			19	
Railways	0·37	13·8		10	7	
Industrial, etc. (d)	1·38	64·6		37	34	
Gas works	0·27	27·2		7	14	
Creosote-pitch		0·7				
	2·54	179·8	Nil	68	93	
Petroleum:						
Fuel gas			7·8			44
Fuel oils	0·58	8·3	2·9	16	4	16
Motor spirits	0·58	5·3	4·7	16	3	26
	1·16	13·6	15·4	32	7	86
Garbage	(e)	(e)	2·5			14
TOTAL	3·7	193	17·9	100	100	100

(a) Department of Statistics (1958).
(b) Committee on Air Pollution (1953, 1954).
(c) Stanford Research Institute (1954).
(d) Includes hospitals, hotels, and institutions.
(e) Not known.

oil-fired boilers used for heating the building. In August 1956, three additional "lead peroxide" instruments were established in the suburbs. One is sited in Aotea Terrace on Huntsbury Hill, approximately 250 ft above mean sea-level and $2\frac{1}{2}$ miles south-east of Cathedral Square. This site is on the fringe of a residential area, generally above fog belts. The second site is in Hinemoa Street, Spreydon, $2\frac{1}{4}$ miles south-west of Cathedral Square, and is surrounded by an extensive residential area. The third site is on the northern boundary of St. Albans Park, $1\frac{1}{2}$ miles north of Cathedral Square, in an extensive residential area.

A deposit gauge and a combined volumetric sulphur dioxide and smoke instrument, similar to those used in Great Britain, are also in operation on the roof of the Government Buildings. The deposit gauge is 14 yards north of the previously mentioned smokestack, and is surrounded by small laboratory buildings and a high limestone and concrete

parapet. The volumetric sulphur dioxide and smoke instrument is in the largest laboratory building with the intake 10 ft above the roof of the main building and 3 ft from the north wall of the laboratory.

Sulphur Dioxide

The evaluation of atmospheric sulphur dioxide in the city area by the "lead peroxide" method covers a period of 4 years. As the results for the first two winters were unexpectedly high and the possibility of interference due to flue gases from the smokestack on the south side of the building could not at that time be excluded, 3 stations were established in the suburbs, and comparative results for the 4 sites now cover 2 years.

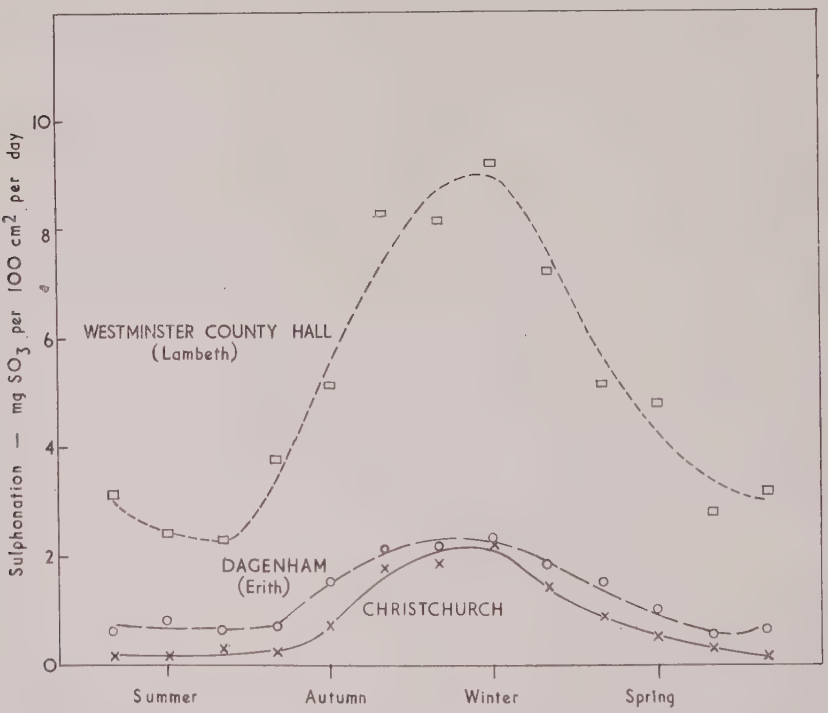


FIG. 1.—Comparison of seasonal effect on incidence of sulphur dioxide in Christchurch atmosphere for 4-year period ended 31 March 1958, with observations at two London sites for 3-year period ended 31 March 1938. Sulphur dioxide measured by the "lead peroxide" method in cowl-type instruments. Values corrected to "Lead peroxide batch A" standard.

Results are recorded in Table 3 in a manner similar to that adopted in the 27th Report on "The Investigation of Atmospheric Pollution" (D.S.I.R. (U.K.), 1955). All results are expressed in terms of "lead peroxide, batch 'A' ", the standard adopted in Great Britain, and have been corrected by a factor of 0·85 to convert results obtained

by exposure under a cowl to those which would be obtained in a "louvred box", the latter now being the standard means of protection in England. All lead peroxide used was calibrated against standard lead peroxide (Batch F) obtained from the Fuel Research Station, England.

For comparison purposes, Table 3 and subsequent tables also include the results from 3 sites in London (D.S.I.R. (U.K.), 1955) and summarized results for Great Britain (D.S.I.R. (U.K.), 1958).

The Lambeth site is the County Hall building, ½ mile from Charing Cross, 80 ft above ground, and the results are the average of two instruments on the roof of this building, which is situated in a commercial and residential district. The Lambeth results are typical of those from districts in the more polluted London areas. Teddington and Erith (Dagenham) are on opposite sides of the Outer Ring, the former being in a residential and parkland district, 11 miles south-west of Charing Cross, and the latter in an industrial area, 11½ miles east of Charing Cross.

The summarized results for Great Britain refer to the year ended 31 March 1956. The "high" values are the arithmetic means for the sites where the 6 highest concentrations, averaged over the whole year, were observed. The "low" values are the arithmetic means for the sites where the 6 lowest concentrations, averaged over the whole year, were observed.

TABLE 3.—Mean Values of Atmospheric Sulphur Dioxide by the "Lead Peroxide" Instrument, Christchurch, London, and Great Britain. All Results in Terms of "Lead Peroxide Batch A" and "Louvred Box" Protection.

City or region	Miles from centre	Mean sulphonation mg $SO_3/100\ cm^2/day$			Ratio: Winter / Summer
		Year	Summer (6 mths)	Winter (6 mths)	
Christchurch:					
City (a)	0	0·76	0·26	1·27	4·9
St. Albans (b)	1½N	0·33	0·11	0·55	5·0
Spreydon (b)	2¼SW	0·42	0·14	0·70	5·0
Huntsbury (b)	2½SE	0·08	0·03	0·12	4·0
London:					
Lambeth 3 and 4 (c)	½SE	2·59	1·57	3·60	2·3
Teddington 2 (c)	11 SW	0·81	0·44	1·18	2·7
Erith 1 (c)	11½E	1·71	1·23	2·19	1·8
Great Britain (d):					
High		7·8	6·5	8·9	
Average		1·87	1·24	2·37	
Low		0·25	0·15	0·35	

(a) Average values for 4-year period ended 30th June 1958—two instruments.
(b) Average values for 2-year period ended 30th June 1958.
(c) Average values for 5-year period ended 31st March 1954.
(d) Values for the year ended 31st March 1956.

Variations in monthly averages for Christchurch (city site) have been compared, in the figure, with similar variations at two London stations (D.S.I.R. (U.K.), 1939).

Systematic daily measurements of sulphur dioxide by the volumetric method were confined to winter months, since occasional determinations at other seasons gave values less than 0·5 part sulphur dioxide per 100 million. Table 4 shows the average and highest daily values for the three winter months recorded during the period 1955 to 1957.

TABLE 4.—Mean values of atmospheric sulphur dioxide by the volumetric method, Christchurch, London, and Great Britain.

City or region	Period	Sulphur dioxide, parts per 100 million by volume	
		Average for three winter months	Highest winter value
Christchurch (city area)	1955 to 1957	6	20
London:			
Lambeth	1949 to 1954	20	134 (a)
Teddington	1952 to 1954	18	89 (a)
Erith	1949 to 1954	4	36
Great Britain:	1955 to 1956		
High		19 (b)	
Average		11 (b)	
Low		3 (b)	

(a) Recorded during London fog episode of December 1952.
(b) Values for a winter period of six months.

Smoke

Smoke measurements were made at the same time as the daily measurement of sulphur dioxide using an apparatus similar to that in the English surveys. The smoke stains were evaluated by comparison with a set of stains calibrated by the National Physical Laboratory, England.

Results of smoke measurements in Christchurch for the three winter months during the period 1955 to 1957 are set out in Table 5.

Deposited Matter

A deposit gauge, differing essentially from the British instrument in type, but not area, of collecting bowl, was installed in May 1955. The results of 13 winter months (10 in the case of dissolved solids) and 5 summer months are available for comparison with English results and are shown in Table 6.

TABLE 5.—Smoke Measurements During Winter, Christchurch, London and Great Britain.

City or region	Period	Smoke, milligrams per 100 cubic metres	
		Average for three winter months	Highest winter value
Christchurch (city area)	1955 to 1957	33	130
London:			
Lambeth	1949 to 1954	42	446 (a)
Teddington	1952 to 1954	14	145 (a)
Erith	1949 to 1954	17	125
Great Britain:	1955 to 1956		
High		81 (b)	
Average		32 (b)	
Low		3 (b)	

(a) Recorded during London fog episode of December 1952.
(b) Values for a winter period of six months.

TABLE 6.—Average summer (S) and winter (W) values of different types of material deposited in Christchurch and London.

Nature of deposit	Average value for deposited matter—grams/100m²/month							
	Christchurch 1955–57		Lambeth 1949–54		Teddington 1949–54		Dagenham 1939–44 (a)	
	S	W	S	W	S	W	S	W
Total solids	421	490	949	1108	418	387	821	876
Undissolved solids	285	310	706	804	257	222	396	389
Dissolved solids	137	180	243	304	161	165	425	487
Ash	232	203	421	464	135	115	240	249
Tar	7	11	13	15	19	21	15	14
Other combustibles	62	96	272	325	103	87	141	126
Calcium, Ca^{++}	9	20	38	40	17	14	—	—
Chlorine, Cl'	23	30	28	43	17	29	59	83
Sulphate, SO_4''	24	69	90	122	43	46	134	157
Magnesium, Mg^{++}	3	7	—	—	—	—	—	—
pH	5·5	4·8	6·3	4·8	5·9	4·8	6·3	5·4

(a) D.S.I.R. (U.K.), 1949

The summarized results of deposited matter found in Great Britain for the year ended 31 March 1956 are shown in Table 7.

TABLE 7.—Deposited Matter: High, Average, and Low Values Obtained in Great Britain, 1955–56.

	Deposited matter, grams/100m²/month					
	High		Average		Low	
Type of deposit	Summer	Winter	Summer	Winter	Summer	Winter
Total solids	3748	4439	691	733	202	187
Undissolved matter ...	2590	2968	421	408	93	65
Dissolved matter	1158	1471	270	325	109	122
pH:						
Maximum	7·3	7·4	—	—	6·8	6·5
Minimum	5·9	5·5	—	—	5·8	5·0

DISCUSSION

In spite of the well documented London fog episode of December 1952 and the vast amount of work being carried out in England and America on air pollution, too little is yet known of the factors in "smog" which are injurious to health. However, it is abundantly clear from the Beaver Reports, a review by Layne (1953), and the Ministry of Health Report (1954), that polluted air is injurious to both physical and mental health.

It is evident from the results in Tables 3 to 7 that, in general, the Christchurch atmosphere is much less polluted with sulphur dioxide, grit, and smoke than is the air in the more polluted parts of London and Great Britain. The differences between the summer and winter concentrations of sulphur dioxide and smoke are, however, far more marked in Christchurch than in England—e.g., Table 3 shows that the winter:summer sulphur dioxide ratio for Christchurch is roughly double that for London. The difference in seasonal effect is no doubt due to a combination of differences in climate and in usage of fuel. The importance of this very marked seasonal cycle to Christchurch citizens, however, is that, during the months of May, June, and July, concentrations of sulphur dioxide and smoke reach levels such as to warrant serious consideration as to their significance.

Table 1 shows that on rare occasions, Christchurch can experience fogs of considerable duration during winter months. The amount of combustible material burnt per square mile in Christchurch is only one-fifth that in London, but half that in Los Angeles. On the other hand, Table 2 shows that the proportion of petroleum products, including petrol, burnt is much higher in Christchurch than in London, and

it is possible that air pollutants from the two sources of fuel, coal and petroleum, may exert a synergistic action pharmacologically. The possibility of a serious "smog" incident occurring in Christchurch appears remote on the evidence at present available. It would be unwise, however, to ignore the probability of long-term effects on health, particularly that of the aged or those suffering from chronic respiratory illnesses.

Apart from injury to health, air pollution has serious economic disadvantages which have been elaborated in the reports of the Beaver Committee (1954) and the Stanford Research Institute (1954). Air pollution causes continuing damage to crops, paint, buildings, metals, textiles, and laundry, and also results in a loss of efficiency.

As coal is still a major factor in the economy of Christchurch, it is worth while considering the feasibility of applying English experience to Christchurch conditions.

The Committee on Air Pollution in its final report (1954) states:

(1) "More than half of all the smoke comes from industrial sources and railways, but for each ton of coal burnt, domestic chimneys produce twice as much smoke as industry and discharge it at a lower level;

(2) "nearly all the grit and dust comes from industrial sources, including power stations and railways;

(3) "sulphur dioxide is discharged wherever coal, coke, or oil is burnt, whether in industrial or domestic premises."

These conclusions are based mainly on the survey work carried out in Great Britain under the guidance of the Atmospheric Pollution Research Committee and published in the periodic "Reports on Observations" (D.S.I.R. (U.K.). The comprehensive report on the scientific survey carried out in Leicester during the years 1937 to 1939 (D.S.I.R. (U.K.), 1945, p. 124) supplies some additional information which enables further comparison of conditions in Christchurch with those in English cities. A correlation between smoke and population was described, and the following empirical rule deduced:

$$\frac{\text{winter mean smoke (mg/m}^3) \times 10^4}{\sqrt{\text{population}}} = 7 \pm 1$$

This rule was found true for 6 English towns and 6 Leicester districts. Three exceptions to this rule were London, where combustion of fuel was considered more efficient than elsewhere, Cardiff, where the practice was to burn low-volatile coals in grates, and Stoke-on-Trent, where industries were considered likely to produce more smoke than the other towns. This rule, applied to the data for Christchurch, gives a figure of 7·8. This is in surprising agreement with English conditions, considering that the *per capita* consumption of coal in New Zealand is about one-third that in Great Britain.

The Leicester report (p. 138) provided another figure of merit, the smoke:sulphur dioxide ratio, which was also used to determine the extent to which coal was burnt smokelessly. The ratios for Leicester and Cardiff were given as 3·1 and 1·0 respectively. Using more recent data obtained from the 27th Report on Observations (D.S.I.R. (U.K.), 1955), the ratios for United Kingdom cities vary from 0·4 to 4·7, but generally lie between 2 and 3. The ratio for Christchurch was found to be 5·5 compared with 2·1 for Lambeth, 0·8 for Teddington, and 4·2 for Erith.

It would appear at first sight that coal may be burnt more smokily in Christchurch than in the average English city. However, the original standard smoke stains, which were used to evaluate stains produced in Christchurch, had been calibrated against London smoke, and the numerical readings obtained locally may therefore not be strictly comparable with English values. In addition, English experience has shown that sulphur dioxide is far more rapidly removed from the atmosphere than is soot, and it is possible that in Christchurch the removal of sulphur dioxide is even more rapid than in England. The nature of the soot measured, and the rate of removal of sulphur dioxide in the Christchurch atmosphere, require further investigation.

As the results of the examination of the deposit gauge material (Table 6) show no major seasonal differences in amounts or nature of the various types of deposit, it can be concluded that in Christchurch, as in England, this instrument provides a measure of the contribution of industry to air pollution. The ash forms a greater part of the suspended solids in Christchurch than is generally the case in England and probably includes a proportion of the wind-blown loess which is a characteristic feature during strong nor'-west winds. The deposit and low summer sulphur dioxide show that the contribution of industry to the general pollution of air in Christchurch is less than the average industrial contribution in England. This is to be expected from a comparison of the industrial development in the two countries.

The high winter values in Christchurch for smoke and sulphur dioxide are therefore largely due to the use of liquid and solid fuels for domestic, industrial, and commercial space heating.

Coal and coke used in domestic grates are estimated to comprise between 40% and 50% of the total coal burned in winter. According to the Beaver report, this means that, in winter, domestic chimneys discharge twice as much smoke at a lower level than do industrial chimneys.

This poses a difficulty in instituting abatement measures which, if a major degree of success is to be obtained, must cope also with the problem of the domestic consumer.

It is estimated that in Christchurch some 50,000 tons of coal, with a cost to the consumer of about £400,000, is burned annually in domestic grates.

Abundant supplies of hydro-electricity are available in the South Island, and it is computed that 50,000 tons of coal burned in domestic grates with an average efficiency of 20% for 6 hours a day during

winter months, is equivalent in heating value to an electric load of 66,000,000 kWh valued at about £200,000. It is estimated that the peak demand would be of the order of 100,000 kW, about $\frac{1}{3}$ of the ultimate installed capacity of the Roxburgh power station. The number of houses burning coal in Christchurch is estimated to be about 50,000. Thus the average annual costs per dwelling for space heating are £8 for coal and £4 for electricity. The capital costs per home in purchasing and installing a 2 kW electric heater would vary from £5 to £30 or more, depending on existing provision of heating points and type of heater. The replacement of coal by electricity in the space-heating of houses is therefore practicable from the point of view of present costs and potential availability of electricity. It would effect a very material reduction in smoke and sulphur dioxide concentrations in the winter atmosphere.

The loss of £400,000 yearly would, however, seriously disturb the economy of the West Coast mining industry. In addition, in spite of the high costs of the modern chimney and coal, the great majority of new homes have at least one fireplace, indicating that most people are not prepared to forgo the emotional pleasure or security given by an open fire.

Considerable reduction in smoke emission and a very considerable increase in heating efficiency (resulting in lower annual costs) can be achieved with the use of smokeless fuels derived from coal and with the installation of the improved open fires and stoves now available. Overall emission of both sulphur dioxide and smoke can be very greatly reduced by replacing coal with gas wherever possible.

Comparative costs and efficiencies of fuel utilization both in England and New Zealand are, however, discussed more fully in the Report (1954) by the Committee on Air Pollution, by Bastings (1958) and by Nicholson (1958). The economic integration of the various sources of energy and its impact on employment and trade are some of the many factors which need to be studied before far-reaching methods to reduce air pollution are adopted.

The problem of emission of sulphur dioxide will remain wherever coal, coke, and fuel oil are burned. The average sulphur content of coal burnt in Christchurch at present is estimated to be about 2%. Much can be done to reduce this emission by coal preparation and selection of low-sulphur fuels. In view of the importance of atmospheric sulphur oxides in regard to soils deficient in sulphur, to erosion of limestone building materials, to corrosion of metals, and to the weathering of paint, the mechanism of the removal of sulphur dioxide from the Christchurch atmosphere needs further elucidation.

The effect of expanding population with changing habits of fuel consumption and of any abatement measures on air pollution in Christchurch can only be evaluated quantitatively by regular measurement of pollution by standardized methods. Such methods need to be sufficiently comprehensive in scope to include also the significant contribution made to the atmosphere by the combustion of petrol and diesel oils in motor vehicles.

Conclusions

(1) The climate and topography of Christchurch, combined with the extensive use of coal for space heating, are conducive to the formation of "smogs" in winter.

(2) The amount of material burnt per square mile in Christchurch is $\frac{1}{2}$ that in Los Angeles and $\frac{1}{5}$ that in London. The particulate and gaseous emissions to the Christchurch atmosphere result from the burning of both coal and petroleum products.

(3) The amount of grit and dust emitted from industrial sources is much less in the Christchurch atmosphere than in the air of the polluted parts of London, and shows little seasonal change.

(4) During the summer months, the Christchurch atmosphere is little polluted with sulphur dioxide and smoke. In winter, however, the incidence of these pollutants is markedly high, although much less in amount than in the polluted London areas.

(5) The high winter values for sulphur dioxide and smoke in Christchurch air are due to the use of fuels for space heating, with the domestic fire as the principal source.

(6) While there is no evidence at present to suggest that dangerous "smogs" are likely to be of frequent occurrence in the future, the present level of air pollution in Christchurch is probably of sufficient potential danger to health and economic importance to warrant further investigation.

(7) Air pollution in Christchurch in winter could be largely reduced by the use of electricity for space heating. Alternatively, the use of more efficient appliances and smokeless fuels derived from coal would reduce the amount of smoke in the air.

Acknowledgements

Thanks are due to Mrs D. Palmer and Miss D. G. Drummond for assistance with analyses; to Mr J. W. Beagley, Geophysical Observatory, D.S.I.R., and Mr A. L. Cullington, Magnetic Observatory, D.S.I.R., for information on fog occurrences; to Miss N. Northcroft, Christchurch Regional Planning Authority, for information on population and area; to Mr W. G. Hughson and Miss J. B. Ross, both of the Dominion Laboratory, Wellington, and to Mr A. J. Lazarus, State Coal Depot, Christchurch, for information on coal supplies.

References

BASTINGS, L., 1958: Handbook on the Insulating and Heating of Buildings. *Dep. sci. industr. Res. N.Z. Inform. Ser. 18.* 71 pp.

Commission of Inquiry into Certain Alleged Nuisances in Districts Within or Contiguous to the Southern Auckland Metropolitan Area (Fumes Inquiry), 1955: *Report.* Government Printer, Wellington. 20 pp.

Committee on Air Pollution (United Kingdom), 1953: *Interim Report.* H.M.S.O., London. 31 pp.

———, 1954: *Report.* H.M.S.O., London. 80 pp.

DAMON, W. A., 1957: Air Pollution in New Zealand. *A Report.* Govt. Printer, Wellington. 23 pp.

DEP. SCI. INDUSTR. RES. (U.K.), 1945: Atmospheric Pollution in Leicester. *Atmosph. poll. Res. Tech. Paper No...1.* 161 pp.

———, 1939: *The Investigation of Atmospheric Pollution, 24th Report.* 117 pp.

———, 1949: *Ibid., 26th Report.* 125 pp.

———, 1955: *Ibid., 27th Report.* 206 pp.

———, 1958: *Ibid., 29th Report.* 123 pp.

DEP. STATISTICS, 1958: "New Zealand Official Year Book". Government Printer, Wellington. 1343 pp.

GRAY, G., 1910: On the Dissolved Matter Contained in Rain Water Collected at Lincoln, New Zealand. *The Canterbury agric. Coll. Mag. 3*: 183–95.

LAYNE, D. A., 1955: A Review on Smog. *J. R. sanit. Inst. 75*: 171–92.

MINISTRY OF HEALTH, 1954: Mortality and Morbidity During the London Fog of December 1952. *Report No. 95.* 61 pp.

NICHOLSON, D. S., 1958: Utilization of Coal in New Zealand, 1920–1955. *Dep. sci. industr. Res. N.Z. Inform. Ser. 19.* 50 pp., 13 figs.

STANFORD RESEARCH INSTITUTE, 1954: The Smog Problem in Los Angeles County. *Report.* Western Oil and Gas Association, Los Angeles.

STEINBERG, S. H., 1958: "The Statesman's Yearbook". Macmillan, London. 1683 pp.

SULLIVAN, J. L., 1957: "An Investigation of Air Pollution Problems in the South Auckland Area". Govt. Printer, Wellington, 27 pp.

SAMPLING OF TIDAL WATERS

By L. WILKINSON, Dominion Laboratory, Department of Scientific and Industrial Research, Christchurch

(Received for publication, 5 January 1959)

Summary

An investigation has been made of the effect of monthly and twice-daily changes in the tides on the composition of the tidal waters of two low-lying rivers flowing into a common estuary with a narrow outlet to the sea. The variations in composition found emphasize the difficulty of obtaining a sequence of comparative samples at times other than low water. The results show that, in assessing the degree of pollution, the mean of a few low-water samples and the mean of a large number of samples taken at all stages of the tide had virtually the same significance.

INTRODUCTION

The Waters Pollution Act 1953 has stimulated awareness of the need for more information regarding the pollutional status of New Zealand waters, and many surveys are now in progress.

Velz (1950) refers to the many factors influencing the sampling of fresh and tidal waters for the effective evaluation of stream pollution. He emphasizes the need for extensive sampling at frequent intervals throughout the daily tidal cycles for the proper evaluation of tidal influences, and on his data the evaluation of the comparative effect of large and small ranges in the tidal phase on bacterial contamination would necessitate about 400 samples for any one sampling point.

Lucht (1953) gives a curve which shows the variations in surface salinity of the Elbe River due to the influence of the tide, and states that this curve seems typical not only of the Elbe estuary but also of other tidal rivers.

Shapiro (1956), in describing the annual pollution survey sampling of New York harbour, states that 1,000 samplings are made each season and that a greater number would be desirable but for limitations on money and manpower necessitating a compromise.

Kaplovsky (1957), on the other hand, compares the information obtained from single midstream samples taken at several sampling points during the low- or high-water slack period of the same tide with that obtained from many cross-sectional samples taken at the same points during several high- and low-water slack periods and at different stages of river flow. He concludes that the results obtained by the "same-slack" sampling procedure provide far more valid data than the cross-sectional technique.

Simmons, Nemerow, and Armstrong (1957) also describe a modified river sampling procedure for computing dissolved oxygen sag. They conclude that the range and distribution of the data collected are more important than the number of samples and that six samples taken under maximum or minimum conditions of one of the three variables of BOD (Biochemical Oxygen Demand), temperature, and flow, are sufficient to provide practical results.

Southgate and Preddy (1952), and Gameson and Preddy (1956) in England, and Ketchum (1950, 1951, 1955) in the United States, have utilized the results of salinity surveys in predictions of the distribution of polluting material in an estuary but do not indicate what variations can occur in salinity.

It was considered that more information concerning the effect of tidal changes on the composition of tidal waters would enable more effective utilization of the limited resources available locally for carrying out pollution surveys.

ESTUARY OF THE AVON AND HEATHCOTE RIVERS

The tidal waters studied were those of the relatively unpolluted Avon River and the grossly polluted Heathcote River which flow through the city of Christchurch situated on a low-lying plain. The two rivers have a common estuary roughly the shape of an equilateral triangle and about 3 sq. miles in area. At the eastern corner the estuary has a narrow outlet to the sea. The Avon and Heathcote rivers enter the estuary at the northern and western corners respectively and at low water flow across the mudflats in separate channels to join near the outlet. The course of the combined outlet channel is subject to frequent change, but the main channels of the two rivers have remained fairly stable over the years.

Estimates of the average amounts of the different waters entering the estuary, based on data given by Bruce (1953) and on information supplied by the Christchurch Drainage Board, are set out below and expressed as cubic feet per tidal cycle:—

Incoming seawater	322,390,000
Returning non-saline water	8,440,000
Avon River	6,540,000
Heathcote River	1,100,000
Sewage farm and ponding area effluents	1,000,000
Other effluents, drains, etc.	1,400,000

Examination of the New Zealand tide-tables (Ruegg, 1953) showed that for the nearby Port of Lyttelton one series of spring and neap tides was predicted for each lunar month, the spring occurring about new or full moon, and the neap about the immediately preceding quarter phase.

Sampling

Sampling stations were established as follows:—

Avon River—Pages Road Bridge

This is 375 chains from the estuary outlet and about 125 chains upstream from the entrance of the estuary. Sewage effluent from the Christchurch Drainage Board's farm and ponding area discharges into the estuary channel of this river about 200 chains downstream from the sampling point.

Heathcote River—Long Street

This is 350 chains from the open sea and 150 chains upstream from the entrance to the estuary. The river is grossly polluted at this point.

Heathcote River—Ferry Road Bridge

This is at the entrance to the estuary, 200 chains from the outlet to the sea.

At Ferry Road the time interval between high and low water is about 6 hr and at the other two stations about $7\frac{1}{2}$ hr.

Samples were taken at $\frac{1}{2}$ hr intervals during daylight hours from the middle of the river and just below the surface.

Tide heights were measured from the bed of the river.

Results and Discussion

Effect of Monthly Tidal Movements on Salinity

The tide height-time curves of the rivers at the three sampling points were approximately sine wave in pattern but with sharply defined peaks and troughs. Only about neap tides did low water heights remain constant for a period of about an hour even though, as at Pages Road, the surface of the river might be from 2 ft to 2·6 ft above the level of the sea during the low water slack.

The Avon at Pages Road was sampled during a period when the tide gauge maintained by the Lyttelton Harbour Board recorded very high spring tides at the last quarter of the moon. During this period there was a linear relation between high water tide height at Pages Road and high water tide height at Lyttelton.

Figure 1 records the chloride concentrations of the samples of the Avon River taken at Pages Road. Unlike the curves for tide height the low water plateaus extended over very considerable periods. On the

day of the unusually high spring tide the plateau covered a period of $3\frac{1}{2}$ hours, whereas on the other sampling days the plateaus covered periods of about 7 hours. About high water the relation between salinity and time was linear.

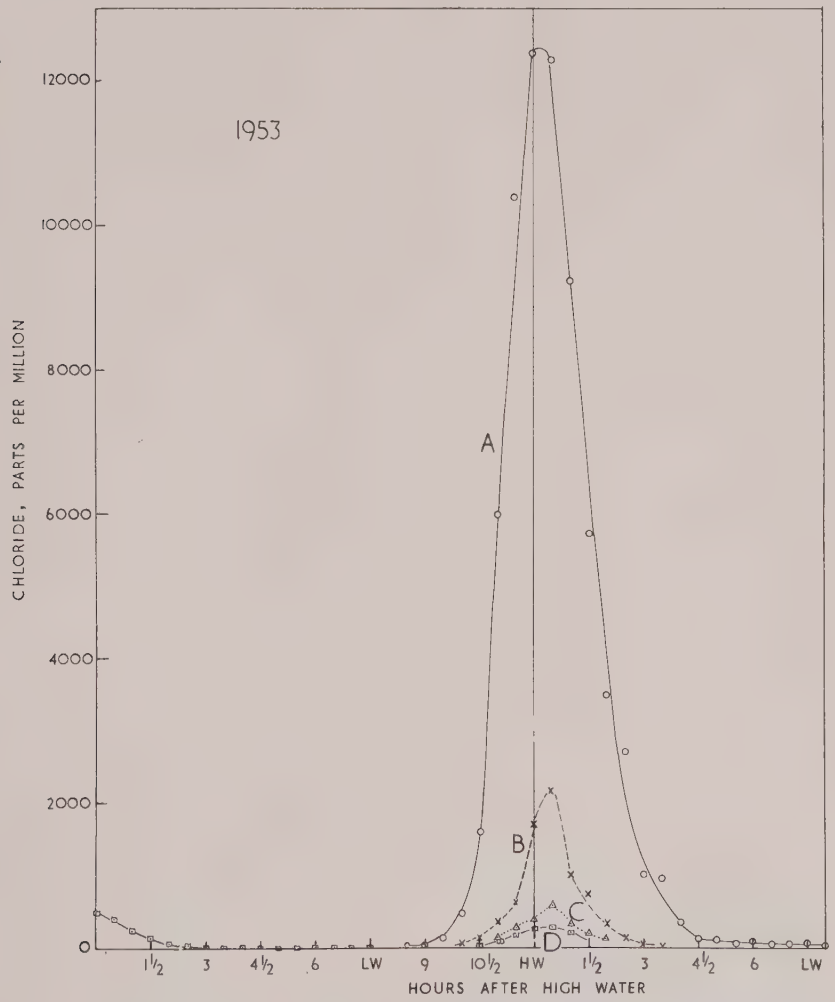


FIG. 1.—Variations in salinity of the Avon River at Pages Road during spring and neap tides. Curve A: 28 Sept.; curve B: 30 Sept.; curve C: 6 Oct.; curve D: 10 Oct.

In Fig. 2 the maximum chloride concentration, expressed as logarithms, for the four tides observed at Pages Road are plotted against the corresponding tide heights. Figure 2 shows that at high water the relation between salinity and tide height is logarithmic.

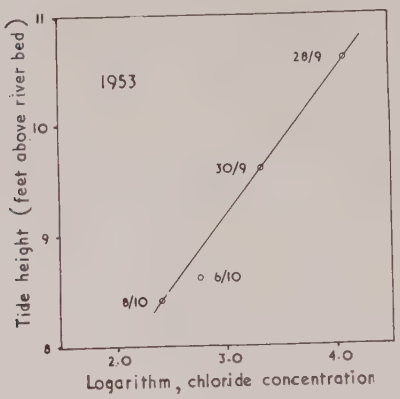


FIG. 2.—Relation between maximum concentration of chloride and tide height of the Avon River at Pages Road for four tides.

Results for the Heathcote River are plotted in Fig. 3 which shows an irregular relation between salinity and time at both sampling points.

At Ferry Road the three salinity-time curves show different patterns about high water and the salinity does not increase smoothly on the flooding tide but in a series of steps. At high water the salinity can be considerably less than at times preceding and succeeding high water, as shown in the curve for 24 June. This pattern and one other was also produced at Long Street but in contrast to the Ferry Road observations the increase in salinity was much more uniform. It is evident that tidal movements across the Estuary were very irregular.

The results show that monthly changes in the tide can effect the proportions of fresh and saline water very considerably.

Changes in Salinity during the Twice-daily Tide

Figure 4 shows the logarithms of the chloride concentrations of the half-hourly Avon samples taken on the 28 and 30 September plotted against tide height. Salinities at tide heights less than 7·5 ft have been excluded for the purpose of simplicity. Both curves exhibit a hysteresis phenomenon, the ebbing tide showing greater salinity than the flooding tide for the same tide height. This was also true for other curves obtained for the Avon and for the Heathcote River at Ferry Road and Long Street. On several occasions maximum salinity occurred on the ebbing tides.

It can be inferred from Fig. 1, 3, and 4 that, with tides showing sharply defined high and low waters, the surface salinity of a tidal river at any particular point can remain fairly constant for a variable period

after low water due to returning river and estuarine water but that at some critical level further increases in tide height result in very marked increases in salinity.

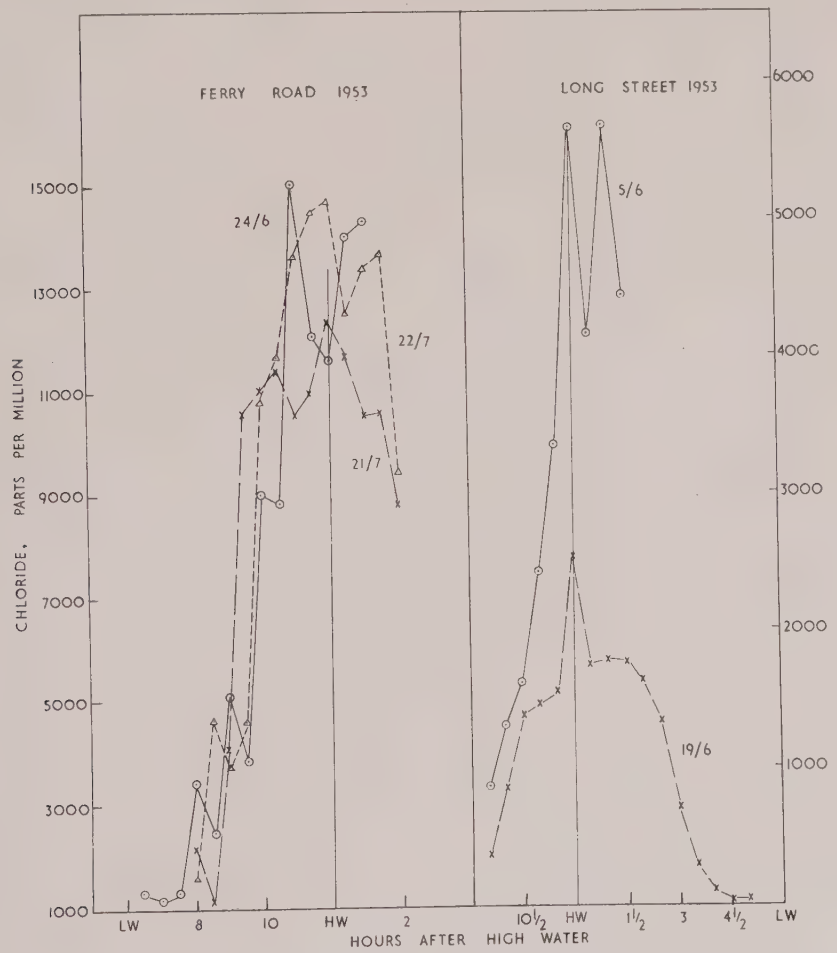


FIG. 3.—Variations in salinity of the Heathcote River during different tides.

Effect of Tidal Changes on the Oscillation of Polluted Estuarine Water

Some information on the effect of monthly and twice-daily changes in the tide on the oscillation of polluted water was obtained by the following method. Sea water is normally low and sewage effluents high in

ammoniacal nitrogen. Other forms of pollution usually contain albuminoid nitrogen. From the salinity, the fresh water content of brackish water can be calculated, and hence the ammoniacal nitrogen content of the non-saline component.

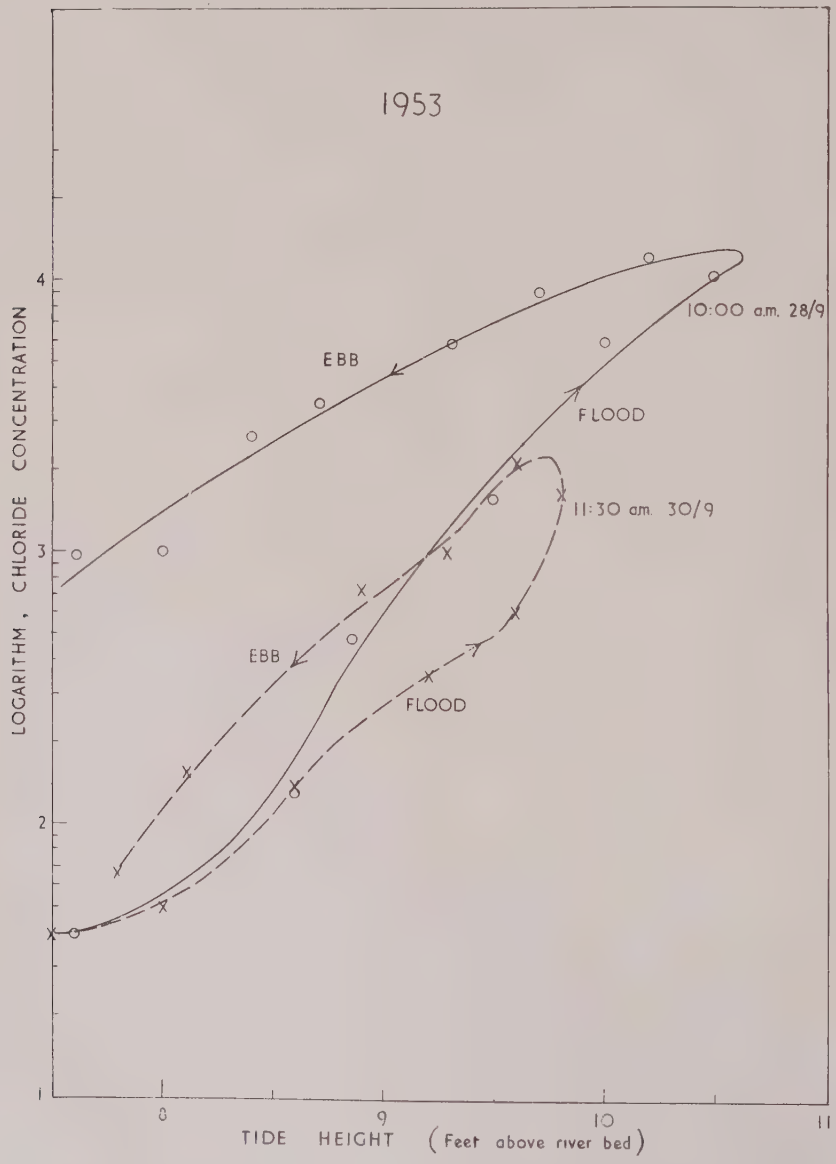


FIG. 4.—Variations in salinity and tide height of the Avon River at Pages Road during flood and ebb of two tides—½-hourly sampling.

Figure 5 shows the effect of different tides on the ammoniacal nitrogen content of the non-saline component of river water at Pages Road.

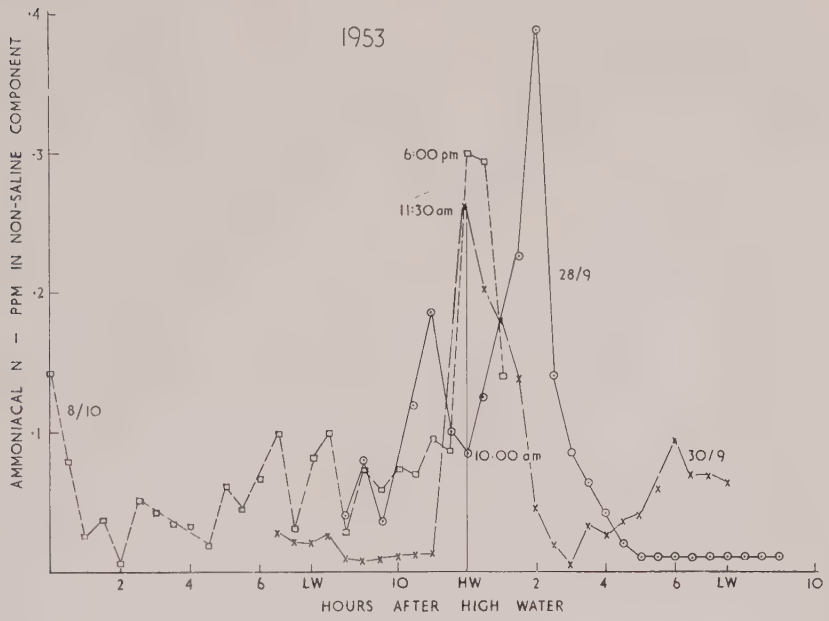


FIG. 5.—Variations in ammoniacal nitrogen values of the non-saline components of the Avon River at Pages Road during spring and neap tides.

Surprisingly, the unusually high spring tide on 28 September appears to have brought up at high water non-saline water relatively low in ammoniacal nitrogen. The explanation for this low nitrogen body of water and other small increases in nitrogen of this tide appears to be in either the possible discharge of very weak sewage effluent during the early morning hours or a considerable measure of stream self-purification. During the early part of the ebb of this unusually high spring tide, some of the non-saline bodies of water were considerably higher in ammoniacal nitrogen than those in the preceding flood.

The results for ordinary spring and neap tides show that it was only at high water that appreciable quantities of more polluted water reached Pages Road.

Figure 6 shows for the Heathcote River at Ferry Road the ammoniacal nitrogen content of the non-saline component during three tidal cycles. No substantial increases in ammoniacal nitrogen were noted after low water. As at Pages Road there was evidence that bodies of

non-saline water low in ammoniacal nitrogen were being brought upstream on the flooding tide. It is doubtful whether any substantial purification of such heavily polluted waters as the Heathcote could occur, and it would therefore appear that this unpolluted water is from the Avon.

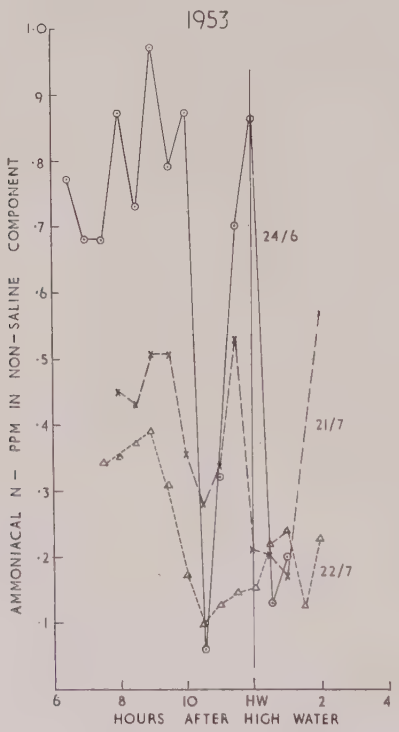


FIG. 6.—Variations in ammoniacal nitrogen values of the non-saline components of the Heathcote River at Ferry Road about high water.

The irregularities found in the chloride and the ammoniacal nitrogen at the three sampling points when the tide is making, at the full, or ebbing, indicate the difficulty in assessing the value of sampling at these times and point to the possibility of considerable stratification of the water during tidal movements.

Validity of Low-Water Sampling

Table 1 compares the mean values of several pollution indices for low and high water and for all stages of the tide at the three sampling stations. Certain of the means have been calculated on the non-saline

TABLE 1.—Comparison of Mean Values of Several Pollution Indices at Low Water and High Water and for All Stages of the Tide.

	Heathcote River						Avon River		
	Ferry Road			Long Street			Pages Road		
	Low water	High water	All stages	Low Water	High water	All stages	Low water	High water	All stages
No. of samples	5	3	92	4	3	90	6	5	106
Chloride (p.p.m.)	1,300	13,000	6,500	44	2,700	800	24	3,040	750
pH	7·3	8·3	7·6	7·3	7·4	7·4	7·2	7·4	7·2
Non-saline component									
Ammoniacal N (p.p.m.)	0·57	0·46	0·47	0·67	0·64	0·79	0·067	0·18	0·069
Albuminoid N (p.p.m.)	0·39	0·71	0·43	0·30	0·49	0·48	0·10	0·25	0·11
Ratio: $\frac{\text{Am. N}}{\text{Alb. N}}$	1·5	0·65	1·1	2·2	1·3	1·7	0·7	0·7	0·6
Oxygen absorbed (p.p.m.)	5·3	7·4	5·9	5·4	6·1	6·1	1·9	1·9	1·6
Impurity figure (Thresh, 1949)	4·6	7·3	5·1	4·2	5·5	5·5	1·5	2·2	1·4
Coliforms at 37° C counts/ml.	160	230	240	220	680	320	19	140	58

component, assuming sea water to have nil values. Sea water does, however, have appreciable oxygen absorbed and substantial but variable amounts of albuminoid nitrogen, and certain of the calculated results will be slightly in error due to these factors.

At Pages Road at high tide the results are somewhat anomalous. There is no clear evidence from either the Long Street or Ferry Road samples that additional pollution is being discharged into the Heathcote River above the former sampling point during high water periods.

In all cases the means of the coliform counts are higher at high water and for all stages of tide than at low water. This is just as likely to be the result of bacterial growth in ageing water as an indication of additional pollution.

The data reveal that a few low-water samples provide almost as much information regarding the incidence of pollution of a tidal water at a particular point for a given period as do many samples taken at all stages of the tide. One disadvantage is that the low water samples may not reveal pollution intentionally discharged at high water when dilution is at a maximum. Evaluation of the condition of a tidal water at other stages of the tide requires, however, a very extensive knowledge of the many local factors that affect tidal movements. Some of these factors cannot be predicted and this increases the difficulty of planning an adequate sampling programme.

ACKNOWLEDGEMENTS

The author is indebted to Mrs F. R. Sharplin and Mr H. G. Ivory, then on the staff of the Dominion Laboratory, Christchurch, for much of the work in sampling and analyses; to the Christchurch Drainage Board and New Brighton Power Boating Club for provision of facilities at the sampling stations; to the Lyttelton Harbour Board and its officers for provision of access to its tide gauge records and to information of tidal movements; to Mr N. P. Alcorn for his interest in the project.

REFERENCES

BRUCE, A., 1953: "Report on the Biological and Chemical Investigation of the Waters in the Estuary of the Avon and Heathcote Rivers". Christchurch Drainage Board, Christchurch. 54 pp.

GAMESON, A. L. H.; PREDDY, W. S., 1956: Factors Affecting the Concentration of Dissolved Oxygen in the Thames Estuary. Public Works and Municipal Services Congress, November.

KAPLOVSKY, A. J., 1957: Estuarine Pollution Investigation Employing "Same-Slack" Technique. *Sewage industr. Wastes 29* : 1042-53.

KETCHUM, B. H., 1950: Hydrographic Factors Involved in the Dispersion of Pollutants Introduced into Tidal Waters. *J. Boston Soc. civ. Engrs. 37* : 296-314.

———, 1951: The Exchange of Fresh and Salt Waters in Tidal Estuaries. *J. Mar. Res. 10* : 18-38.

———, 1951: The Flushing of Tidal Estuaries. *Sewage industr. Wastes 23* : 198-209.

———, 1955: Distribution of Coliform Bacteria and Other Pollutants in Tidal Estuaries. *Ibid. 27* : 1288-96.

LUCHT, F., 1953: Hydrographic Studies of the Zone of Brackish Water in the Estuary of the Elbe River. *Dtsch. hydrogr. Z. 6* : 18-32.

RUEGG, H., 1953: "New Zealand Nautical Almanac and Tide-Tables". Government Printer, Wellington. 251 pp.

SHARPIRO, R., 1956: Pollution Survey Sampling of New York Harbour. *Sewage industr. Wastes 28* : 1504-6.

SIMMONS, J. D.; NEMEROW, N. L.; ARMSTRONG, T. F., 1957: Modified River Sampling for Computing Dissolved Oxygen Sag. *Sewage industr. Wastes 29* : 936-43.

SOUTHGATE, B. A.; PREDDY, W. S., 1952: Discharge of Sewage and Industrial Wastes to Estuaries. *J. R. sanit. Inst. 72* : 424-38.

THRESH, J. C.; BEALE, J. F.; SUCKLING, E. V., 1949: "The Examination of Waters and Water Supplies". 6th ed. (edited by Taylor, W.), p. 277. Churchill, London. 819 pp.

VELZ, C. J., 1950: Sampling for Effective Evaluation of Stream Pollution. *Sewage industr. Wastes 22* : 666-84.

TOXICITY OF SOME ARSENICAL WOOD-PRESERVATIVES TO THE COMMON HOUSE BORER, *ANOBIUM PUNCTATUM* DE GEER

By K. M. HARROW, Plant Diseases Division, Department of Scientific and Industrial Research, Auckland

(Received for publication, 3 April 1959)

Summary

Tests have shown that the toxicity of three arsenical wood-preservatives, Boliden S 25 (zinc-copper-chrome-arsenate), Tanalith C (copper-chrome-arsenate), and Tanalith U (fluor-chrome-arsenate-phenol), to the common house borer, *Anobium punctatum* De Geer, is proportional to their arsenic content. The toxicity of arsenic combined in these different preservative mixtures was equal to that introduced into the wood as arsenic pentoxide, which shows that the other elements present (Cr, Cu, Zn, F, and dinitrophenol) did not contribute to the toxicity to *Anobium* larvae, nor did they reduce the availability of arsenic in the wood. Larvae were able to survive at retentions of 0·01% As_2O_5 on an oven-dry wood basis, but retentions of 0·018% As_2O_5 prevented their development.

INTRODUCTION

Two recently introduced wood-preservatives, Boliden S 25 and Tanalith C, designed primarily against fungous decay under severe exposure conditions, are also being used in New Zealand to treat building timbers. It was of interest, therefore, to determine their toxicity to the common house borer, *Anobium punctatum* De Geer, the prevalent pest of sapwood timber in New Zealand buildings. The opportunity was taken, also, to accumulate further evidence of the activity of arsenic contained in multi-salt wood-preservatives, and two additional materials, arsenic pentoxide and Tanalith U, were included in the tests.

Boliden S 85 was supplied as a paste by the New Zealand agents, C. M. Malfroy Ltd. The sample was stated to have the following anhydrous composition: As_2O_5 48·3%, ZnO 15·5%, CuO 5·2%, CrO_3 31·0%. The whole sample was dissolved in water to prepare a stock solution containing 1·0% As_2O_5.

Hickson's Timber Impregnating Co. (N.Z.) Ltd. supplied:

(a) a 5% stock solution of Tanalith C having a stated composition $K_2Cr_2O_7$ 42·6%, $CuSO_4.5H_2O$ 36·9%, $As_2O_5.2H_2O$ 20·5%.

(b) a 5% stock solution of Tanalith U having a stated composition Na_2CrO_4 39%, Na_2HAsO_4 23·5%, NaF 25·3%, dinitrophenol 12·2%.

(c) a 0·36% stock solution of arsenic pentoxide, As_2O_5.

Samples of these stock solutions and treating solutions prepared from them were assayed for arsenic by the Dominion Laboratory. The results reported agreed very closely with the stated arsenic contents.

METHOD

Test blocks $1\frac{1}{2}$ in. $\times$ 1 in. $\times$ $1\frac{1}{4}$ in. long were sawn from two air-dry (18% M.C.) sapwood boards of kahikatea, *Podocarpus dacrydioides* A. Rich., designated (a) and (b). Blocks weighing 10·4 to 10·9 g were selected for treatment. They were impregnated by the method (Harrow, 1954) of evacuating, flooding, and soaking under atmospheric pressure using solution concentrations based on an unexpected solution absorption of 200% oven-dry block weight. The absorption obtained ranged about 190%.

The dry-salt loadings (percentage on oven-dry wood weight) are shown in the table of results.

The Tanalith U loadings were arranged on the assumption that the fluoride contributed to the toxicity and were based on Spiller's (1948) finding that, at loadings of 0·042% Tanalith and below, *Anobium* larvae were able to survive.

To test the susceptibility of the timbers used, a group of water-impregnated control blocks from both boards were included in the test. Following impregnation, blocks were air-dried on racks before being placed individually in 4 oz jars fitted with screw caps. At the flight period, 25 unsexed *Anobium* beetles were placed in each jar. Eight months later, the blocks were taken from their jars, examined for egg cases, and then sectioned on a microtone so that live larvae, if present, could be observed.

RESULTS

Egg-laying was heavy on all test blocks. None had fewer than 100 eggs, and the untreated controls were found to be infested with many live larvae when examined. The results of treatments are shown in Table 1.

With arsenic pentoxide alone, live larvae were found at loadings of 0·01% As_2O_5 and lower, while at loadings of 0·018% As_2O_5 and higher all larvae had died. When the loadings of the three multi-salt preservatives are expressed as As_2O_5, a toxicity level identical with that of arsenic pentoxide is found.

In terms of total salt, the following minimum toxic loadings to *Anobium* larvae were determined:

Anhydrous Boliden S 25	.....	between 0·043% and 0·023%
Hydrated Tanalith C	.....	between 0·017% and 0·051%
Anhydrous Tanalith U	.....	above 0·073%

DISCUSSION

The highest retention at which live larvae were found, 0·1% As_2O_5, was the same as that previously reported for the zinc-chrome-arsenate preservative, Boliden BIS-S (Harrow, 1954). It would therefore seem conclusive that arsenic acts independently as a poison to *Anobium*

TABLE 1.—Toxicity of Arsenic Pentoxide, Boliden S 25, Tanalith C, and Tanalith U to Larval *Anobium punctatum*.

Arsenic Pentoxide

Block loading expressed as % As_2O_5	Survival of larvae						
	0·0023	0·0046	0·0070	0·010	0·018	0·027	0·044
Timber:							
Kahikatea (a)	++++	++++	++++	+OO+	OOOO	OOOO	OOOO
Kahikatea (b)	++++	++++	++++	++++	OOOO	OOOO	OOOO

Boliden S 25

Block loading expressed as							
(a) % Total anhydrous salt	0·0055	0·011	0·017	0·023	0·043	0·067	0·086
(b) % As_2O_5	0·0023	0·0046	0·007	0·010	0·018	0·028	0·036
Timber:							
Kahikatea (a)	++++	++++	++++	++OO	OOOO	OOOO	OOOO
Kahikatea (b)	++++	++++	++++	+++O	OOOO	OOOO	OOOO

Tanalith C

Block loading expressed as							
(a) % Total hydrated salt	0·013	0·026	0·039	0·051	0·107	0·152	0·282
(b) % As_2O_5	0·0023	0·0046	0·0069	0·009	0·019	0·027	0·050
Timber:							
Kahikatea (a)	++++	++++	++++	OOO+	OOOO	OOOO	OOOO
Kahikatea (b)	++++	+O++	++++	+O+O	OOOO	OOOO	OOOO

Tanalith U

Block loading expressed as						
(a) % Total anhydrous salt	0·027	0·037	0·048	0·056	0·073	
(b) % As_2O_5	0·004	0·005	0·007	0·008	0·01	
Timber:						
Kahikatea (a)	++++	++++	++++	O+++	O++O	
Kahikatea (b)	++++	++++	++++	++OO	OOOO	

\+ denotes block with live larvae present O denotes block with live larvae absent

larvae and is not assisted by the presence of substantial quantities of copper, zinc, dinitrophenol, or fluoride. Also, the availability of arsenic as a poison is not affected by being introduced into the wood with chrome, which is generally considered to "fix" arsenic in a non-leachable, insoluble form.

REFERENCES

HARROW, K. M., 1954: Toxicity to Boliden Salt BIS-S, Copper Sulphate, and Celcure to the Common House Borer, *Anobium punctatum* De Geer. *N.Z. J. Sci. Tech. B 36*: 277–80.

SPILLER, D., 1948: Toxicity of Wolman Tanalith to the Common House Borer, *Anobium punctatum* De Geer. *Ibid., B 30*: 140–2.

CONSTITUENTS OF *PHYLLOCLADUS GLAUCUS*

By E. G. BROOKER,* Department of Chemistry, University of Auckland

(Received for publication, 13 February 1959)

Summary

Phyllocladene has been isolated from the leaves of *Phyllocladus glaucus*. Acetic and ferulic acid esters of the bimolecular compound of ceryl and lignoceryl alcohols have been obtained from both the root and aerial barks.

INTRODUCTION

Phyllocladus glaucus is a small tree (25 to 40 ft high) endemic to New Zealand, where it is sparsely distributed over the northern areas of the North Island. The steam volatile oils of the other New Zealand species, *P. alpinus* (Briggs, 1937; Brandt, 1938) and *P. trichomanoides* (Briggs and Sutherland, 1948) and the Tasmanian species, *P. rhomboidalis* (Baker and Smith, 1910), have all yielded phyllocladene. Steam distillation of the leaves of *P. glaucus* has now given phyllocladene. Insufficient leaves were available for a large-scale distillation, but such a distillation may have yielded terpenes and sesquiterpenes, in addition to phyllocladene, as was shown to be the case with *P. alpinus* (Brandt, 1938).

Extraction of the aerial and root barks of *P. glaucus* with methanol gave low-melting waxes consisting mainly of esters of acetic and ferulic acids with a high molecular weight aliphatic alcohol. Analyses indicated the formula $C_{25}H_{52}O$ for the alcohol, but the melting-point, in conjunction with the rarity of odd-numbered carbon alcohols in natural products, suggests that the alcohol is the bimolecular compound of lignoceryl ($C_{24}H_{50}O$) and ceryl ($C_{26}H_{54}O$) alcohols described by Warth (1947).

Although ferulic acid has been identified in numerous leaf hydrolysates (Bate-Smith, 1954) and has frequently been isolated as the free acid from plant materials (Bamberger, 1891; Tschirch and Knitl, 1899; Hiramoto and Watanabe, 1939; Akkerman and Veldstra, 1947; Karrer, Eugster, and Patel, 1949; Kurth, 1950), there does not appear to be any well authenticated report of its isolation as an ester of this type. Kurth (1950) has shown that it probably occurs in the bark of *Pseudotsuga taxifolia* (Douglas fir) as a lignoceryl ester, but he did not isolate it as such.

---

*Present address: New Zealand Forest Products Ltd., Penrose, Auckland.

EXPERIMENTAL

Analyses were made by Dr A. D. Campbell, University of Otago, and Dr R. C. Cooper, Auckland Institute and Museum, carried out the botanical identification.

Isolation of Phyllocladene

Air-dried leaves of *P. glaucus* (660 g) collected at Huia in March were steam distilled, yielding an oil which partially solidified on cooling (0·745 g; 0·11%). Crystallization from ethanol afforded phyllocladene, m.p. and mixed m.p. 94°–95° C, $[\alpha]_D^{23°}$ + 14·6° (*c* 1·16 in chloroform) and an infrared spectrum (in KBr) identical with that of authentic phyllocladene. A portion isomerized by heating with ethanolic sulphuric acid (Briggs, 1937) gave *iso*phyllocladene, m.p. and mixed m.p. 110°–111° C.

Extraction of Bark

Air-dried aerial bark (127 g) was extracted (Soxhlet) with 85% aqueous-methanol for 5 days and on concentration of the extract a waxy brown solid (3·737 g; 2·9%) was obtained. A benzene solution of this material was chromatographed on alumina (100 g) and elution with benzene yielded a colourless wax (0·251 g) which, after crystallization from methanol gave colourless plates, m.p. 53°–54° C (Found: C, 79·1; H, 13·3. Calc. for $C_{27}H_{54}O_2$: C, 79·0; H, 13·3%), λ_{max}^{EtOH} 220 mμ (log ε 2·39). The infrared spectrum (in KBr) had maxima at 2941, 1742, 1466, 1366, 1205, 1174, 1049, 970, 907, 731, and 727 cm^{-1} consistent with an aliphatic ester. After saponification with 10% ethanolic potassium hydroxide for 2 hr, a crystalline product was obtained which recrystallized from acetone as balls of needles, m.p. 77°–78° C (Found: C, 81·8; H, 14·2. Calc. for $C_{25}H_{52}O$: C, 81·4; H, 14·2%). The infrared spectrum (in KBr) had maxima at 3330, 2941, 1462, 1362, 1067, 976, 952, 928, and 727 cm^{-1} consistent with an aliphatic alcohol. Acetylation with acetic anhydride-pyridine at room temperature overnight gave the acetyl derivative which crystallized from methanol in colourless needles m.p. 55·5°–57° C, undepressed on admixture with the original ester.

Further elution of the column with chloroform gave a colourless wax (1·045 g), which after crystallization from methanol formed thin irregular plates, m.p. 63·5°–64·5° C (Found: C, 77·0; H, 11·3. $C_{35}H_{60}O_4$ requires C, 77·2; H, 11·1%), λ_{max}^{EtOH} 236 and 328–330 mμ (log ε 3·97 and 4·25). This compound decolorized bromine in chloroform solution and gave a bright yellow colour with aqueous alkali. The infrared spectrum (in KBr) had maxima at 3472, 2967, 2857, 1706, 1634, 1608, 1520, 1433, 1279, 1214, 1174, 1160, 1126, 1035, 982, 936, 849, 821, and 729 cm^{-1}. After saponification with 10% ethanolic potassium hydroxide, the product which separated on cooling crystallized from acetone as colourless plates, m.p. and mixed m.p. with the aliphatic alcohol described above, 75°–77·5° C (Found: C, 81·9; H, 13·8; Calc. for $C_{25}H_{52}O$: C, 81·4; H, 14·2%). The infrared spectra of the two alcohols

were identical. Ether extraction of the acidified filtrate from the saponification mixture gave a light brown solid which on crystallization from water gave colourless needles of ferulic acid, m.p. and mixed m.p. 169°–171° C (Found: C, 61·9; H, 4·9; Calc. for $C_{10}H_{10}O_4$: C, 61·9; H, 5·2%) λ_{max}^{EtOH} 214 and 320 mμ log ε 4·36 and 4·19), identical with an authentic specimen. Karrer, Eugster, and Patel (1949) record λ_{max} 218 and 322 mμ (log ε 4·11 and 4·24).

Examination of the root bark gave similar results.

ACKNOWLEDGEMENT

The author is indebted to Professor L. H. Briggs for his continued interest and encouragement.

REFERENCES

AKKERMAN, A. M.; VELDSTRA, H., 1947: *Rec. Trav. chim. Pays-Bas. 66*: 411.

BAKER, R. T.; SMITH, H. G., 1910: "Pines of Australia". N.S.W., Govt. Printer, Sydney; p. 419.

BAMBERGER, M., 1891: *Mh. Chem., 12*: 452.

BATE-SMITH, E. C., 1954: *Chem. & Ind. (Rev.)*, 1457.

BRANDT, C. W., 1938: *N.Z. J. Sci. Tech., B 20*: 88.

BRIGGS, L. H., 1937: *J. Soc. chem. Ind., Lond., 56*: 137T.

BRIGGS, L. H.; SUTHERLAND, M. D., 1948: *J. org. Chem., 13*: 1.

HIRAMOTO, M., WATANABE, K., 1939: *J. pharm. Soc. Japan, 59*: 261.

KARRER, P.; EUGSTER, C. H.; PATEL, D. K., 1949: *Helv. chim. acta, 32*: 2397.

KURTH, E. F., 1950: *J. Amer. chem. Soc., 72*: 1685.

TSCHIRCH, W. O. A.; KNITL, A., 1899: *Arch. Pharm., Berlin, 237*: 258.

WARTH, A. H., 1947: "The Chemistry and Technology of Waxes", Reinhold Publishing Corporation, New York; p. 11.

THE SOLUBILIZATION OF "INSOLUBLE" PHOSPHATES:

V—THE ACTION OF SOME ORGANIC ACIDS ON IRON AND ALUMINIUM PHOSPHATES

By H. W. Johnston, Imperial Chemical Industries (N.Z.) Ltd., Wellington, New Zealand

(Received for publication, 2 February 1959)

Summary

From a study of the action of some organic acids on ferric and aluminium phosphates, it appears that acid structure influences the interaction with these two "insoluble" phosphates. Citric acid is more powerful than hydrochloric or any other organic acid used on either form of phosphate.

For iron phosphate, oxalic, tartaric, and malic acids in that order follow citric in their actual phosphate release, followed by α-hydroxy monobasic acids. With aluminium phosphate, malic, oxalic, and α-hydroxy monobasic acids follow citric and precede tartaric in this same capacity.

Introduction

Having found that structure could affect appreciably the action of organic acids on tricalcium phosphate (Johnston, 1954a & b; Johnston and Miller, 1959), the writer decided to extend the investigation to iron and aluminium phosphates. Knowledge gained about the action of organic acids on these phosphates would be of interest in soil chemistry since these two elements are regarded as the main converters of "available" phosphate to "unavailable" phosphate in acid soils.

Since the exact nature of iron and aluminium phosphates in soils is as yet unknown, the experiments were carried out with laboratory reagent forms of these phosphates.

For the purposes of this investigation, it was deemed sufficient to see what acids would react to what extent with these phosphates and whether structure had any influence at all on the amount of phosphate released. No comparison is made between the results obtained from the action of these acids on iron phosphate and those from aluminium phosphate since it is almost certain that the laboratory forms differed in cation:phosphate ratio and also in their active surface area.

There is an acute paucity of published information on the action of organic acids on either of these phosphates. Seifert (1932) in a study of "cloudiness" in wine-making reported that malic acid would dissolve more ferric phospate than either tartaric or lactic acids.

EXPERIMENTAL TECHNIQUE

The technique was the same as that used previously with tricalcium phosphate (Johnston, 1954a and b). An aliquot of standard acid was shaken with an excess of phosphate for 48 hours at 20° C. The mixture was allowed to settle, centrifuged, and then filtered through a membrane filter to give a clear filtrate. A 2 ml aliquot of this filtrate was taken and a colorimetric phosphate determination made as described previously. Salicylic acid, being insoluble in water, was used as outlined before (Johnston, 1954b).

Where possible, the acids were of Analytical Reagent Grade (A.R.): those not of this standard were purified to constant melting point. The figures quoted for malic acid are the average of five determinations for the iron salt and six for the aluminium.

RESULTS

Results are presented in Table 1 and Fig. 1. The results of the interaction of each organic acid with either iron or aluminium phosphate are expressed as milligrams of P_2O_5 in 100 ml of filtrate, using the amount of phosphate released as an index of the extent of reaction with each organic acid used.

TABLE 1.—Phosphate Released by Organic Acids from Ferric and Aluminium Phosphates.

Acid used	Phosphate released—mg P_2O_5/100 ml filtrate	
	$FePO_4$	$AlPO_4$
Hydrochloric	40	88
Citric	440	300
Oxalic	200	114
Tartaric	165	67
Malic	165	173
Mandelic	64	83
α-Hydroxyisobutyric	62	98
Lactic	50	110
Salicylic	33	68
Furoic	28	20
Phthalic	23	13
Acetic	18	Negligible
β-Hydroxybutyric	18	Negligible
Propionic	17	Negligible
Butyric	15	Negligible
Succinic	15	Negligible

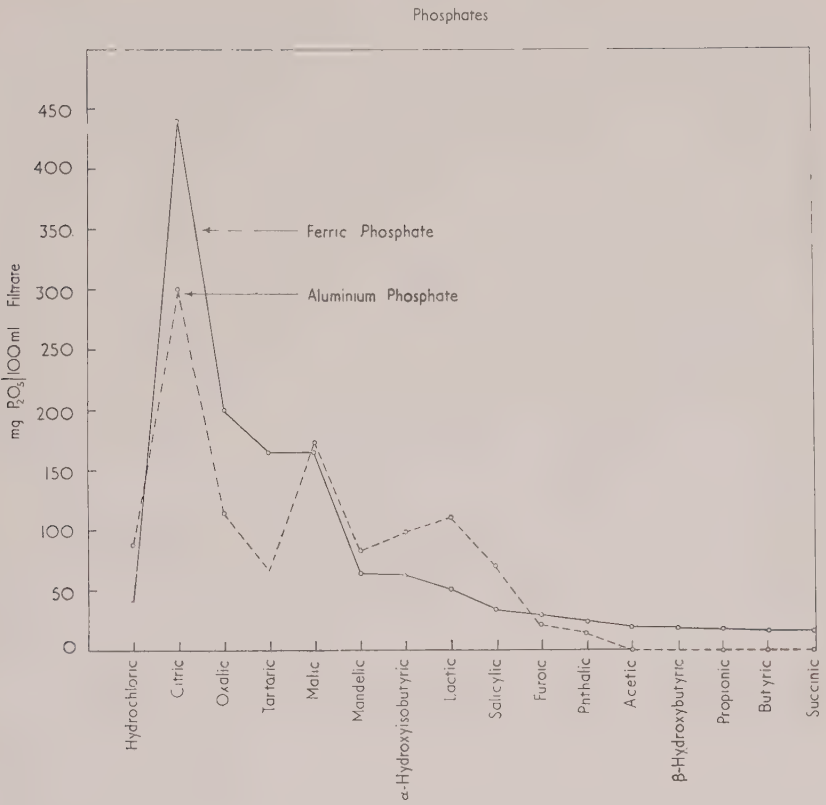


FIG. 1.—For reasons mentioned in the text, this graph is not for comparison of results obtained, but is presented to show visually the pattern of the effect of acid structure on the release of phosphate from each "insoluble" phosphate used.

DISCUSSION

The effect of structure can be seen in the interaction of the acids with both ferric phosphate and aluminium phosphate.

In the case of ferric phosphate, the first significant point is the extent to which citric acid can release phosphate. The second is the marked superiority of citric acid over hydrochloric acid. It is quite evident that hydroxy derivatives (except β-hydroxybutyric) are much more effective in attacking ferric phosphate than their unsubstituted parent acids. This applies equally to dibasic and monobasic acids. Compare

lactic and propionic
mandelic and acetic
α-hydroxyisobutyric and butyric
malic and succinic
tartaric and succinic.

With aluminium phosphate, citric also released the most phosphate of any acid used. The order of effectiveness after citric is such that no clearly defined pattern of structure emerges. Malic and then oxalic acids are next in line followed by a group of three α-hydroxy monobasic acids. Below these is tartaric which for some unaccountable reason releases about half the amount of phosphate that malic does, in spite of the fact that they are so similar in structure. Weaker still than tartaric are the unsubstituted acids.

If oxalic acid is excluded, it appears that hydroxy acids release more phosphate from aluminium phosphate than their unsubstituted parent acids, providing it is not β-substitution for a monobasic acid.

CONCLUSIONS

By comparing the action of organic acids on iron and aluminium phosphates, it has been shown that—

Many organic acids release more phosphate from each of these compounds than hydrochloric does;

Of the organic acids, citric is the strongest in its action on either form of phosphate;

Among dibasic acids, hydroxy derivatives are stronger in releasing phosphate than their unsubstituted parent acid;

The same principle applies for monobasic acids; and for one acid, α-substitution is superior to β-substitution.

ACKNOWLEDGEMENTS

The writer takes this opportunity of thanking former associates in the Soil Bureau, Department of Scientific and Industrial Research, Wellington, for their assistance and interest throughout this work.

REFERENCES

JOHNSTON, H. W., 1954a: The Solubilization of Insoluble Phosphates: II A Quantitative and Comparative Study of the Action of Chosen Aliphatic acids on Tricalcium Phosphate. *N.Z. J. Sci. Tech., B.36* : 49-55.

———, 1954b: The Solubilization of Insoluble Phosphates: III A Quantitative and Comparative Study of the Action of Chosen Aromatic Acids on Tricalcium Phosphate. *N.Z. J. Sci. Tech., B.36* : 281-4.

JOHNSTON, H. W.; MILLER, R. B., 1959: The Solubilization of Insoluble Phosphates: IV: The Reaction between Organic Acids and Tricalcium Phosphate. *N.Z. J. Sci. 2* : 109-20.

SEIFERT, W., 1932: The Solubilities of Ferrous and Ferric Phosphates in Solutions of Organic Acids and their Relation to the so-called Gray Break of Wines. *Öst. Chem-Ztg. 35* : 30-4.

AN AUTOMATIC APPARATUS FOR THE LUNDEGARDH METHOD OF ANALYSIS

By J. E. Allan and O. E. Clinton, Rukuhia Soil Research Station, Hamilton, New Zealand

(Received for publication, 6 February 1959)

Summary

An apparatus is described for the automatic flaming of solutions in the Lundegårdh method of analysis.

Introduction

The well established Lundegårdh method of spectrochemical analysis is applicable to about 30 elements which are excited in the flame, and has been widely used during the past twenty years, particularly for the analysis of agricultural materials (Mitchell, 1948). Although now superseded to some extent by methods of direct flame photometry for the determination of such elements as K and Na for which a simple filter flame photometer is adequate, the method is still of use for other elements which emit in the flame, particularly where a flame photometer of the quartz monochromator type is not available.

The actual technique of spraying the solution to be analysed into an air acetylene flame, and of recording the resulting spectrum on a photographic plate is simple, but tedious and time consuming. With the conventional Lundegårdh apparatus, the time required to flame 58 solutions—sufficient for one plate—and to process the plate is at least $2\frac{1}{2}$ hr, and constant attention to these operations is required. For plate reading and calculation of results, most conveniently done by two operators, about $\frac{1}{2}$ hr per element is required. There is considerable advantage therefore in the mechanization of the flaming procedure. Lundegårdh built a "Robot" capable of carrying out the complete operation automatically, and a brief description of this machine is available in the English translation of his book. (Lundegårdh, 1951). On account of its size and the amount of solution required, particularly for duplicate analysis, it was considered that a Lundegårdh "Robot" would not be suitable for use in this laboratory. A machine has therefore been constructed which is both compact and portable, and can therefore be conveninetly removed from the spectrograph when either is required for other work. Incorporated in the machine is a modification of Lundegårdh's atomizer, requiring substantially less solution for an analysis.

DESCRIPTION OF APPARATUS

Atomizer and Burner

Before mechanization could be undertaken, it was necessary to modify the Lundegårdh atomizer and burner. With the original atomizer, changing solutions involved disconnecting the spray chamber, an operation obviously difficult to mechanize. Lundegårdh overcame this difficulty by altering the spray chamber, so that by a series of operations controlled by an electromagnetic valve, the old solution could be drained out, the chamber flushed first with distilled water then with 25 ml of the new solution, and finally the new solution for spraying poured in. As this required a total of between 30 and 35 ml of solution for each analysis, an investigation was made of the various types of atomizer used in flame photometry, that draw up solution directly from a beaker. After considering the requirements of economy of solution, sensitivity, and freedom from blockages, it was found that these could best be met by a modification to the Lundegårdh atomizer.

To enable the solution to be taken by directly from a sample bottle, a $\frac{1}{2}$ in. length of stainless steel capillary tube (19SWG) was inserted in the intake hole of the atomizer and fixed in position by soldering through a threaded brass plug which screwed into a reinforcing collar. Small-bore rubber tubing was used to extend the length of the tube to about 4 in. (Fig. 1). The tip of the atomizer was inserted into a spray chamber, the outlet of which was connected to the burner by a rubber

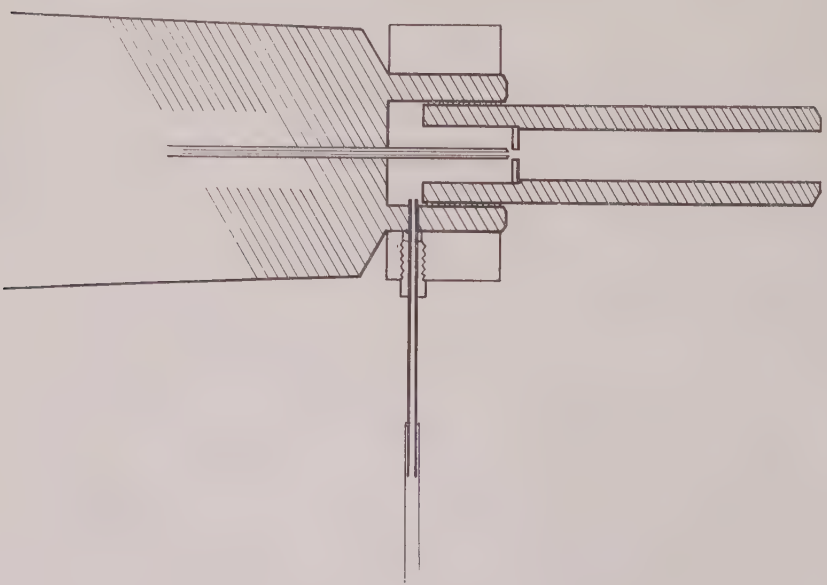


FIG. 1.—Modified Lundegårdh Atomizer.

tube, having a drain trap at its lowest level. With this arrangement, sample changing simply required one bottle to be substituted for another, while the amount of solution required for analysis was about 7 ml. As it did not appear possible for a solution, once it had condensed on the walls of the spray chamber, to reach the flame, it was expected that it would not be necessary to rinse the spray chamber between samples, and that, provided sufficient time was allowed for the spray from the new solution to completely replace that from the old, no contamination from the previous sample would occur.

This was checked experimentally by flaming a solution which was 25 times as concentrated as the highest standard and measuring the light intensity with a filter, photocell, and galvanometer. The solution was then replaced by distilled water, and it was found that the galvanometer reading fell to a previously obtained distilled water reading in about 12 to 15 sec. As with the original atomizer, the sensitivity was as good as, or better than that of other atomizers tried, and blockages were rare.

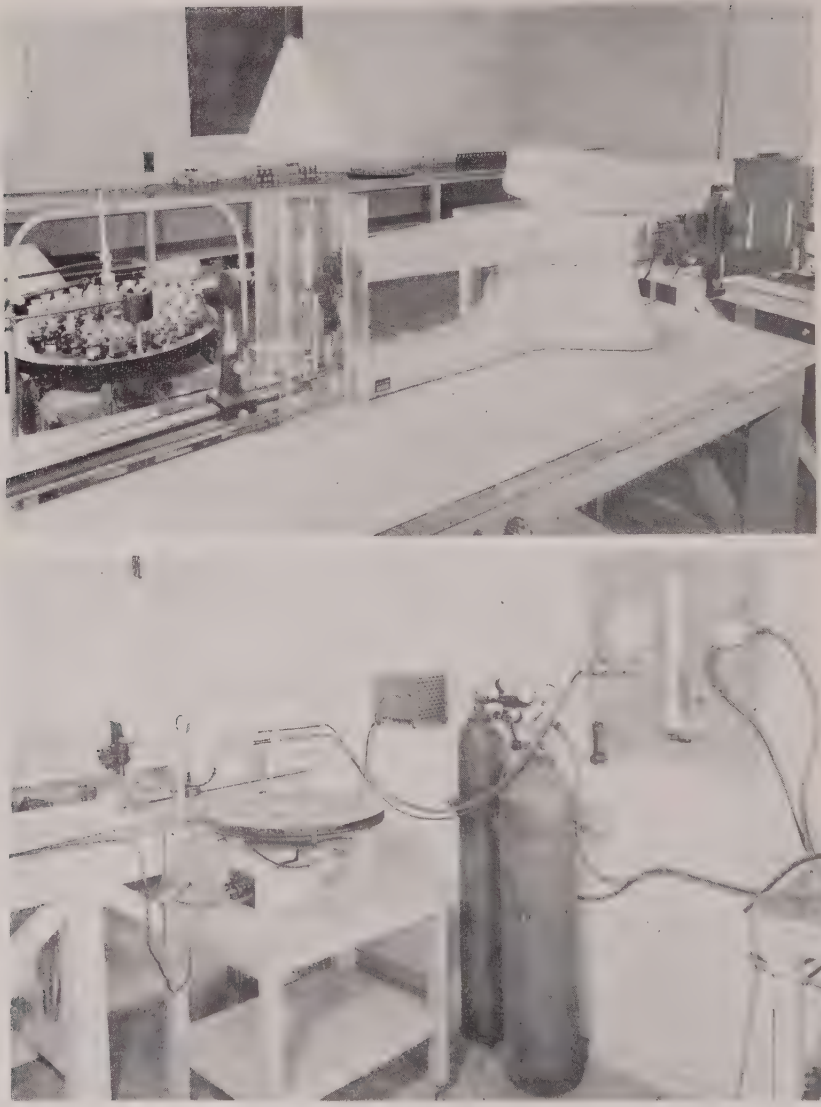
With the original Lundegårdh burner, difficulty was experienced in maintaining a constant acetylene flow due to partial blockage of the acetylene jet with condensed spray. In manual operation, this could be overcome by using a flowmeter in the acetylene line, instead of the usual manometer, and adjusting the flow when necessary, but this, of course, is not satisfactory for an automatic system. Enlarging the acetylene jet is not a solution to the problem, as the lower velocity of acetylene leads to inefficient mixing of the acetylene and air, and hence an unstable flame.

The acetylene was therefore introduced through a large tube into the spray chamber, where the high air velocity was sufficient to ensure thorough mixing. The spray chamber was made of polythene rather than glass to eliminate any danger in the event of a flash back from a burner. With this arrangement, the usual type of single stage regulating valve on the acetylene cylinder was sufficient to maintain a constant flow of acetylene through the burner for long periods of time. The air was obtained from a compressor, the pressure being sufficiently controlled by a double stage regulator.

With the stability of gas and air supply assured, and sample changing simplified to the lowering of one bottle and the raising of another in its place, mechanisation of the flaming procedure could be carried out.

Automatic Machine

A general view of the whole arrangement in use with the spectrograph, in this case a Hilger medium quartz instrument, is shown in Figs 2a and b. The apparatus consists of three parts, a shutter, a sample-changing machine, and a plate-racking mechanism. The sample-changing machine, on which are mounted the atomizer and spray chamber, consists essentially of a turnable, on which is placed a tray



FIGS 2a and b.—General views of automatic apparatus.

carrying the sample solutions in bottles, and a lever mechanism for raising and lowering the bottle. Each bottle in turn is lifted when beneath the capillary, held for a fixed time during which the exposure is made, then lowered back into its position on the tray. This change-over from one sample to the next, and the movement of the plate-holder which occurs during this time, is initiated by the shutter which also times the exposure.

As 58 spectra can be recorded on a 4 in. plate when using a spectrograph slit length of $1\frac{1}{2}$ mm, the tray accommodates up to 58 bottles. Provision is made for the replicate flaming of samples and for the return of the plateholder and turntable to the starting position when the set has been completed.

THE SHUTTER is mounted on the Lundegårdh burner stand in front of the slit of the spectrograph, and consists of a disc, $2\frac{1}{2}$ in. in diameter, driven by a 230 v. A.C. synchronous motor (Synclox 1 r.p.m.) geared down to rotate at 0·75 r.p.m. Attached to this disc is a quarter sector which is interposed between the flame and the slit at the end of the 60 sec. exposure period. When this occurs, a pin mounted on the shutter disc momentarily closes a micro switch (S1 in Fig. 4). This initiates the operation of the sample-changing machine and the plate-racking mechanism. During the change-over of samples, the rotation of the shutter is stopped, and does not start again until the new sample is in position. (This ensures that should any fault occur in the bottle-changing mechanism, the whole operation comes to a standstill). After the new sample is in position and the shutter starts to rotate again, 20 seconds elapse before the slit is exposed to the light from the new sample. This is sufficient time for the spray from the old sample to be completely replaced by that from the new.

THE SAMPLE-CHANGING MACHINE is built on a trolley so that it can readily be moved when not required. Details of the construction can be seen in Fig. 3, to which the letters in the following description refer. A compartment on top houses the relays and a small electric motor. A shaft coupled to this motor through a reduction gear to give a shaft speed of 18 r.p.m., with a simple sprung plate clutch, carries three cams which actuate the micro switches S2, S3, and S4 shown in Fig. 4. The end of the shaft protrudes through the front of the compartment and drives the lifting cam (A), which is coupled to a vertical lift rod (B) by means of a lever (C). The lift rod runs freely between two pairs of roller bearings (D), and has a flat rubber-covered top, 1 in. in diameter, to carry the sample bottle. A guide (E) is provided to prevent the bottle falling should it topple, and should the bottle stick for any reason, the clutch slips and prevents damage to the machine.

Three parallel $\frac{1}{4}$ in. diameter rods (F) are fixed to the top of the compartment, in such a way as to provide rails for the forward movement of the carriage (G). Attached to the carriage are three rollers (H) which support the turnable (I) at equidistant points around the rim. The turntable, which rotates about a central spindle, consists of a disc of $\frac{1}{2}$ in. plywood and is rim driven by a small electric motor sprung-mounted on the carriage.

Through the disc are 58 holes, $1\frac{1}{8}$ in. in diameter, spaced at 2 in. centres around $2\frac{3}{4}$ turns of a linear spiral of the form $r = 4$ in. $+ \theta/180$. Screwed to the underside of the turntable disc is a raised $\frac{1}{4}$ in. square

section copper track (J) on a spiral of the same form but with $r = 5$ in. $+ \theta/180$. This track passes between two small rollers (K) attached to a block on the front centre of the compartment, and positioned at a distance forward from the lift rod, equal to the distance between the hole centres and the track. These rollers cause the forward movement of the carriage as the turntable rotates, and thus keep the line of holes accurately above the lift rod.

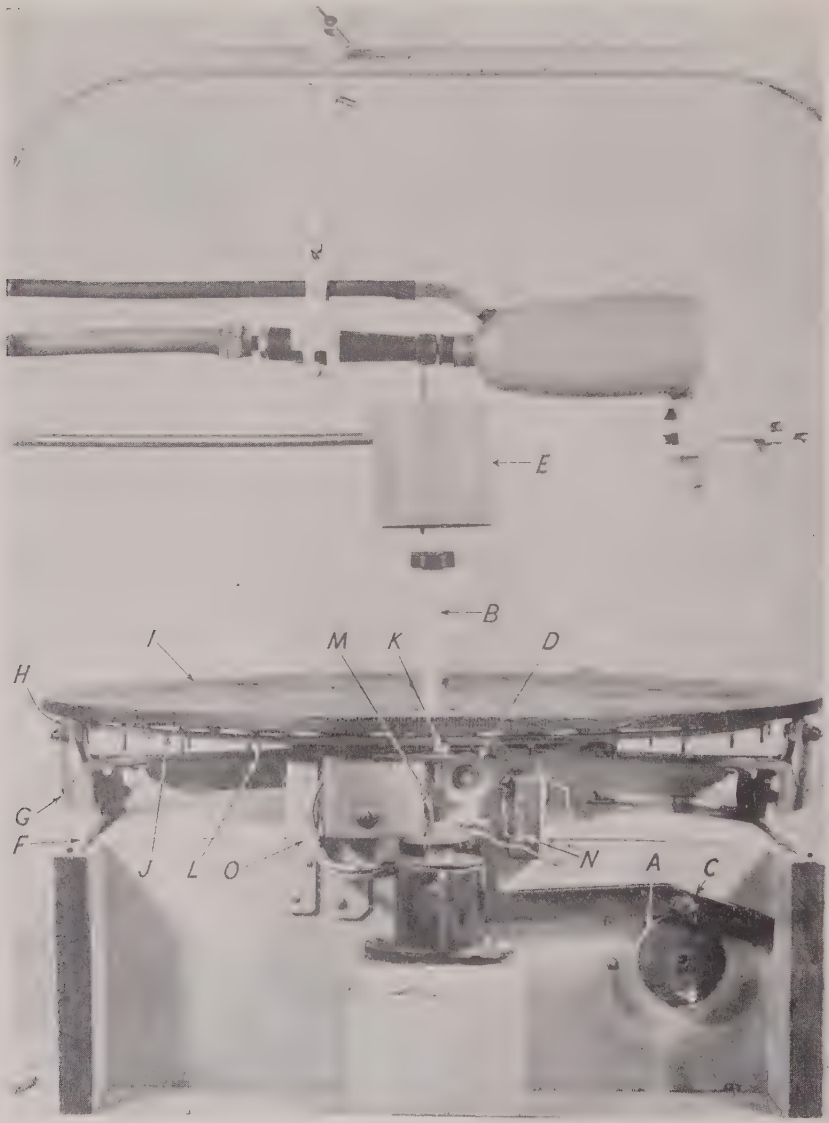


FIG. 3.—Details of bottle-changing machine. (For explanation see text.)

Adjacent to the holes, brass pins (L), 1in. by $\frac{1}{8}$ in., are set into the copper spiral track at 2 in. intervals. These pins, when in contact with a solenoid armature (M), which travels vertically in the space between the small rollers, close an electrical circuit which stops the turntable motor. At the same time, the presence of the solenoid armature, which is supported from behind by a block, prevents further movement at the turntable, and ensures that it is accurately positioned with a hole above the lift rod. This is necessary, as the momentum of the turntable with its load of bottles is too great for it to be stopped at precisely the right place by the motor brake alone. When changing from one sample to the next, the solenoid circuit is closed so that the armature is pulled down, thus releasing the pin and allowing the turntable to rotate. As this rotates, the pin comes into momentary contact with a small leaf spring, causing the solenoid circuit to be opened so that the armature springs up again to arrest the turntable on contact with the next pin. Electrical contact with the copper spiral, and hence the pins, is made by carbon brushes bearing on the flange of the turntable spindle to which the end of the spiral is attached. The solenoid armature is connected to the electrical circuit simply by means of a flexible wire.

The samples are carried in 60 ml bottles in a wooden tray which is placed on the turntable and located by two pins, so that the $1\frac{1}{8}$ in. holes in the lower surface are lined up with those in the turntable. The bottles sit in $1\frac{3}{4}$ in. diameter holes drilled from the upper surface to a depth of about $\frac{7}{8}$ in., thus leaving a base of about $\frac{1}{8}$ in. thickness, through which the $1\frac{1}{8}$ in. holes are drilled.

Provision is made for replicating a set of exposures on the same plate. A plug, which protrudes below the turntable, is placed in the tray after the last bottle. Further rotation causes the plug to close a micro switch (N) which reverses the turntable to the starting position, where a pin, attached to the turntable, actuates another micro switch (O), which causes the normal forward operation to begin again.

THE PLATE-RACKING MECHANISM consists of a small electric motor mounted by means of a bracket to the camera base of the spectrograph. A $3\frac{1}{2}$ in. gear is fixed to the existing plate-racking control, and meshes directly with a $\frac{3}{4}$ in. gear on the motor shaft. A micro switch fixed to the bracket tracks on the inside edge of the larger gear, where appropriately spaced holes cause the switch to operate, stopping the motor at 1·5 mm. intervals of plate travel. The motor bracket can be shifted slightly to disengage the gears and permit manual racking of the plate carrier when the spectrograph is used for other work. The small amount of run-on that occurs is sufficiently constant to avoid overlapping of the spectra on a plate. The electrical circuit is so arranged that, should the micro switch be opened through over-run, the motor does not start.

At the limit of plate travel, a micro switch mounted on the spectrograph is actuated by the plate carrier and reverses the plate motor so that the plate carrier returns to the start position where it is stopped by the action of a second micro switch.

THE ELECTRICAL CIRCUIT is shown in Fig. 4. S1–S9 are micro switches of which S5 and S9 are the normally closed type. A–I are relays of which B, C, E, F, G, and H have latches. S13 represents the contact between the pin and the solenoid armature, while S14 represents the contact between the pin and leaf spring. L is the solenoid coil and M1 is the 230 v. A.C. synchronous timing motor.

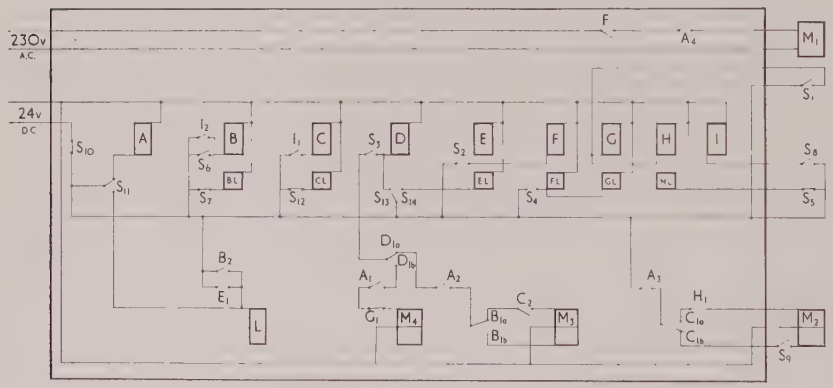


FIG. 4.—Electrical circuit.

The use of a 24 v. D.C. system was decided upon because of the ready availability of components from aircraft dismantled after the war. The motors used (M2–M4) were from aircraft landing lights and had magnetic brakes, built in reduction gears to give a final shaft speed of 160 r.p.m., and with two field windings, were reversible. They were thus admirably suited for their present use. The relays and solenoid were likewise obtained from aircraft. A 24 volt 6 amp. rectifier unit is sufficient to operate the whole system.

At the commencement of operation the circuit is as shown in Fig. 4, i.e. relays G, F, and C are down and latched, hence G1 is closed, F1 open, C1b closed, and C2 open. The cam-operated switches S2, S3, and S4 are open. S7 is closed and S9 is open.

The sequence of events is as follows:

(1) When S10 is closed, relay A closes, hence contacts A1-A4 close, thus connecting the motors to the automatic circuit.

(2) Momentary closure of the push button switch S12 closes the latch CL, so that the relay C opens, thus closing C1a and C2. The turntable motor M3 starts and the turntable rotates. S7 opens, thus opening the latch BL.

(3) The turntable continues to rotate until the pin adjacent to the first bottle comes into contact with the solenoid armature S13. This closes relay D. D1a opens and the turntable stops. D1b closes and the cam motor M4 starts. As the camshaft rotates, the cam-operated switch S3 closes and the sample bottle is lifted. When the bottle has reached the highest position, the cam switch S4 closes.

(4) The closure of S4:

(a) closes GL, so that relay G opens, thus opening G1, and the cam motor stops.

(b) closes FL, so that relay F opens, thus closing F1, and the timing motor M1 starts.

(5) After 20 seconds, the $\frac{1}{4}$ sector driven by the timing motor is removed from the light path and the exposure commences. At the end of the 1 minute exposure, the sector is again interposed between the flame and the slit. S1 is then momentarily depressed by the pin on the timing disc.

(6) The closure of S1:

(a) closes relay H, so that H1 closes and the plate motor M2 starts. As M2 runs, S5 opens, HL is released and latches relay H. M2 continues to run until the plate reaches its next position, when S5 closes, closing HL and thus allowing H to open. (By this time S1 has opened.) The opening of relay H opens H1 and the plate motor M2 stops.

(b) closes relay G so that G1 closes and the cam motor M4 starts and commences to lower the bottle. Cam switch S4 opens, so that GL opens and latches relay G.

(7) As the bottle is lowered, cam-operated switch S2 closes and:

(a) closes relay F which is latched. F1 opens and the timing motor (M1) stops.

(b) closes relay E which is latched. E1 closes so that the solenoid coil (L) is energized, the armature is pulled down, and the contact S13 broken. Relay D is now held by S3. (See (3) above.) S2 now opens.

(8) When the bottle has been lowered to its position in the tray and the lift rod has reached its low position, the cam-operated switch S3 opens, thus opening relay D so that D1b opens and the cam motor stops. D1a closes and the turntable motor starts.

(9) As the turntable revolves, the pin makes a momentary contact with the leaf spring S14, so that EL closes allowing relay E to open, thus opening E1 and de-energizing the solenoid so that the armature springs up.

(10) The turntable continues to revolve until the pin adjacent to the next sample bottle contacts the solenoid armature S13. This closes relay D and the whole process is repeated from (3) above.

Replicate exposures are made by placing a plug in the tray after the last bottle. This plug protrudes through the bottom of the tray, so that as the turntable revolves, the plug closes a micro switch S6 (N in Fig. 3). This closes relay B, which is latched. Contact B2 closes so that the solenoid armature is pulled down, B1a opens and B1b closes, and the turntable motor reverses. It continues to rotate in the reverse direction until the first sample is passed, when a micro switch S7 (0 in Fig. 3) is closed by a pin on the turntable. This closes BL, allowing relay B to open. B2 opens so that the solenoid armature springs up. B1b opens and B1a closes, and the turntable goes forward again until the first pin contacts the solenoid armature, and so on from (3) above. In this way a set of samples may be repeated as often as required, provided there is room on the plate.

After the 58th exposure, further movement of the plate carrier closes a micro switch S8. This closes relay I and:

(a) I1 closes so that relay C closes and is latched. C1a opens and C1b closes so that the plate motor reverses and the plate carrier is returned to the starting position, where the micro switch S9 is opened and the plate motor stops.

(b) C2 opens.

(c) I2 closes so that relay B closes and is latched. B2 closes and the solenoid armature is pulled down. B1a opens and B1b closes causing the turntable to reverse and run back to the start position where the micro switch S7 is closed, closing BL, and allowing B to open, thus opening B1b and closing B1a. The turntable motor stops, because, unlike the situation described above for the repeat process, C2 is open.

The situation is now as it was at the beginning, and the whole procedure can be initiated by closing S12 as in (2) above.

In order to make the unit more flexible in operation and faults more easily corrected, a set of manually operated switches not shown in Fig. 4 is provided. When S11 is in the down position, the solenoid coil circuit is complete and at the same time, the voltage is applied to the manual switches and through them to the three motors which are disconneced from the automatic circuit by the opening of relay A. Manually operated switches are also provided in parallel to S6 and I1 and across F1 and A4.

Conclusion

As the whole operation described above requires about 1½ hours for 58 exposures, up to 348 spectra can be recorded in a working day with only part time attention of the operator. During the 1½ hour period, there is ample time to process the previous plate and set out the subsequent set of bottles on a tray so that the machine can operate continuously.

This apparatus has been in use at the Rukuhia Soil Research Station for the past five years, has handled many thousands of samples satisfactorily, and enabled the analyses to be done with a minimum of manpower. Initially the apparatus was used in the conventional Lundegårdh method mainly for the determination of K, Ca, Na, Mg, and Mn in agricultural materials, and occasionally for the determination of other elements such as Cu, Fe, Sr, etc., in a variety of materials. Latterly, the bottle-changing machine has been used in conjunction with a 4-channel flame photometer with which K, Ca, Na, and Mg are determined simultaneously. When used in this way, the changing of samples is initiated by a manually operated switch in parallel with S1. This has been found of great convenience to the operator, who, freed from the necessity of changing samples by hand, can concentrate on recording the galvanometer readings.

Acknowledgement

The authors gratefully thank Mr D. F. Waters for his constant interest and many useful suggestions.

References

MITCHELL, R. L., 1948: The Spectrographic Analysis of Soils, Plants, and Related Materials. *Tech. Commun. Bur. Soil Sci. Harpenden, 44.*

LUNDEGARDH, H., 1951: "Leaf Analysis" (translated by R. L. Mitchell). Hilger Watts Ltd., London.

THE EXTRACTIVES OF *VITEX LUCENS* T. KIRK

PART 2—THE LEAVES AND BARK

By R. C. CAMBIE, Department of Chemistry, University of Auckland

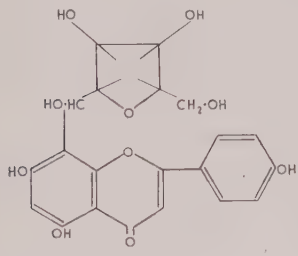
(Received for publication, 20 November 1958)

Summary

Vitexin has been isolated from the bark of *Vitex lucens* and its absence in the leaves has been shown by paper chromatography. Pentatriacontane, stearic acid, β-carotene, and p-hydroxybenzoic acid have been shown to be present in the leaves, while β-sitosterol and a mixture of saturated aliphatic alcohols, the principal one of which is "ceryl" alcohol, have been isolated from the bark.

INTRODUCTION

During an investigation of the structure of the flavonoid pigment, vitexin (I), isolated from the sapwood and heartwood of *Vitex lucens* (New Zealand "Puriri") by Briggs and Cambie (1958), an examination of the leaves and bark for possible occurrence of vitexin, appeared of interest.



(I)

Extraction of the leaves with light petroleum followed by column chromatography of the concentrate gave three major fractions. Pentatriacontane and stearic acid were obtained from the first and second fractions, respectively, while the third fraction, a bright orange band on the column, was shown to contain β-carotene by measurement of the ultraviolet spectrum in two solvents. From an ether extract of the leaves p-hydroxybenzoic acid was isolated (0·05% yield) by extraction with sodium hydrogen carbonate. This acid has also been isolated from the leaves of the related species *Vitex negundo* by Ghose and Krishna (1936).

Paper chromatographic examination of a methanolic extract of the leaves showed the presence of three flavonoid constituents (Table 1) none of which appeared to be identical with either vitexin or isovitexin, when run as control. No clear separation was achieved by attempted chromatography in 60% aqueous acetic acid on cellulose columns and no spot corresponding to either vitexin or isovitexin appeared when a butan-1-ol extract of the hydrolysate was examined by paper chromatography. An ether extract of the hydrolysate gave a further yield (0·2%) of p-hydroxybenzoic acid.

A light petroleum extract of the bark gave a solid which was separated by column chromatography into two major fractions. One fraction, eluted with benzene contained a mixture of saturated aliphatic alcohols, the principal fraction of which was purified by re-chromatography and identified as "ceryl" alcohol (0·04% yield). Polland, *et al.* (1931) have shown that "ceryl" alcohol is a mixture containing mainly hexacosan-1-ol. The second fraction, eluted with ether, was identified as β-sitosterol, previously isolated from the heartwood by Briggs and

TABLE 1.—Flavonoid Constituents of the Leaves.

Substance	R_f values†		Colour on paper‡		
	BAW	5% HAc	UV	NH_3	UH:NH_3
Spot 1	0·23	0·06	B-P	Y	B-G
Spot 2	0·36	0·16	B-P	Y	B-G
Spot 3	0·78	0·50	—	Y	B
Vitexin	0·63	0·14	B-P	Y	B-G
Isovitexin	0·76	0·28	B-P	Y	B-G

†Average of 4 determinations.
‡B = brown, G = green, P = purple, Y = yelow.

Cambie (1958). No crystalline compounds were isolated by attempted working up of an ether extract of the bark and no useful results were obtained by attempted chromatography on alumina.

The concentrate from a methanolic extract of the bark was stripped of ethyl acetate and butan-1-ol soluble material and each fraction and the methanol soluble residue were examined by paper chromatography (Table 2). The ethyl acetate extract contained two non-flavonoid compounds which were also present in the butan-1-ol extract but no solid was isolated by chromatography of the ethyl acetate extract on alumina. Both the butan-1-ol fraction and the methanol-soluble residue contained three major flavonoid components, two of which appeared to be identical with vitexin and isovitexin respectively, and which were still present after hydrolysis of the fractions.

When extracting the wood of *Vitex lucens* (formerly *Vitex littoralis*) Evans *et al.* (1957) were able to isolate vitexin without prior hydrolysis. No vitexin was obtained from the original methanolic concentrate of the bark in the present investigation, by the method of Evans *et al.* It was, however, isolated in low yield (0·01%) after hydrolysis by the method of Briggs and Cambie (1958). Glucose was the only sugar detected in the hydrolysate by paper chromatography. It would appear that vitexin exists mainly in the form of a glucoside in the bark extract. Paper chromatographic examination of a methanolic extract of the sapwood of *Vitex lucens* showed, among a complex series of spots, two faint spots corresponding to those of vitexin and isovitexin, respectively, and which were considerably strengthened after hydrolysis.

TABLE 2.—Paper Chromatographic Data in the Bark.

Band*	R_f values†		Colour on paper‡		
Ethyl acetate extract	BAW	5% HAc	NH_3	UV:NH_3	Spray reagent
1	0·82	0·41	Bl	Bl	B-O
2	0·84	0·48	O	O	B-O
Butanol extract					
1	0·22	0·04	Y	B-G	B
2	0·63	0·13	Y	B-G	B
3	0·76	0·28	Y	B-G	B
4	0·82	0·41	Bl	Bl	B-O
5	0·84	0·48	O	O	B-O
6	—	0·64	Bl	Bl	B-O
Methanol extract					
1	0·22	0·04	Y	B-G	B
2	0·63	0·14	Y	B-G	B
3	0·76	0·28	Y	B-G	B

*R_f values for faint bands are not recorded.
†Average of 4 determinations.
‡B = brown, Bl = blue, G = green, O = orange, Y = yellow.

This would indicate that both vitexin and isovitexin do occur free in the wood in trace amount but does not explain the considerable yield of vitexin (0·5%) isolated by Evans *et al.* before hydrolysis. This discrepancy could, however, arise by partial hydrolysis during extraction of their wood sample.

Examination of the extracts for alkaloids, with the usual reagents, showed their absence in the bark and only faint traces in the leaves. Tests indicated the absence of anthocyanins in the leaves.

EXPERIMENTAL

Analyses were by A. D. Campbell, University of Otago. Infrared spectra were measured as KBr discs with a Beckmann IR2 instrument.

Paper chromatographic investigation of flavonoid constituents was carried out by the methods of Jurd, Geissman and Seikel (1957) and Seikel and Geissman (1957), using the solvent systems, butanol-acetic acid-water (100:27:73) and 5% aqueous acetic acid. The spray reagent was diazotised p-nitroaniline.

The Leaves

Fresh leaves (955 g) of *Vitex lucens* were air-dried for three weeks, finely ground and successively extracted (Soxhlet) with light petroleum (b.p. 50° to 60°), ether and methanol, each extraction for 32 hr.

LIGHT PETROLEUM EXTRACT

The green oily concentrate from the extract was chromatographed in benzene on alumina (Brockmann II). Elution with benzene separated a bright orange band from chlorophyll and leaf xanthophylls. Rechromatography of the combined concentrated orange eluants on alumina (Brockmann I) gave three major fractions:

(a) *Fraction 1*: Addition of a few drops of ethanol to the colourless oily concentrate gave a waxy hydrocarbon mixture, m.p. 68·5° to 70·5° (evac. tube), further purified by removal of unsaturated impurities by repeated treatment with hot concentrated sulphuric acid. The insoluble wax after repeated crystallization from benzene-methanol formed glistening plates (12 mg), m.p. 74° to 75° (evac. tube). [Found, for sample dried at room temperature to constant weight: C, 85·4; H, 14·6%; *M* (Rast), 501. Calc. for $C_{35}H_{72}$: C, 85·4; H, 14·6%; M, 493.] [Power and Moore (1910) record m.p. 74° to 75° for pentatriacontane.] The infrared spectrum showed peaks at 2962 ($-CH_3$), 2872 ($-CH_3$), 1466 ($-CH_2-$), 1377 ($C-CH_3$) and 725 cm^{-1}.

(b) *Fraction 2*: Trituration of the pale yellow oily concentrate with ethyl acetate gave a discoloured solid (0·54 g), soluble in sodium hydroxide but insoluble in aqueous sodium carbonate .Repeated crystallization from benzene gave colourless plates of stearic acid, m.p. and mixed m.p. 69° to 69·5° (evac. tube). [Found: C, 76·2; H, 12·7. Calc. for $C_{18}H_{36}O_2$: C, 76·0; H, 12·%.] The p-toluidide formed plates (from ethanol), m.p. and mixed m.p. 101° to 102°.

(c) *Fraction 3*: The dark orange oil from this fraction was further chromatographed in benzene on alumina (Brockmann II). A single orange band which was readily eluted with benzene gave an oil which could not be readily crystallized. The ultraviolet spectrum in n-hexane showed maxima at 425 mμ (inflection), 451 mμ and 483 mμ and in chloroform showed maxima at 466 mμ and 498 mμ. [Goodwin (1955) records λ max. 425 (inflection) mμ, 451 mμ and 483 mμ in n-hexane and λ max. 466 mμ and 497 mμ in chloroform, for β-carotene.] The fraction gave a green-blue colour with concentrated sulphuric acid and a dark blue colour with boron trifluoride.

ETHER EXTRACT

The gummy concentrate from the extract was redissolved in ether and extracted repeatedly with aqueous sodium hydrogen carbonate. The extracts were acidified, filtered from black insoluble material and the filtrate re-extracted with ether. Removal of solvent from the dried solution gave a brown gum containing crystalline material. The solid was separated from insoluble impurities by extraction with hot water. Recrystallization from water (charcoal) gave clusters of granular tablets of p-hydroxybenzoic acid (0·55 g), m.p. and mixed m.p. 215° to

216°. [Found: C, 61·2; H, 4·2%; *M* (Rast), 146, 146. Calc. for $C_7H_6O_3$: C, 60·9; H, 4·4%, *M*, 138.] $\lambda_{max.}^{EtOH}$ 263mμ log ε 4·16). The infrared spectrum showed carboxyl bands at 2688, 2551, 1680, 1420, 1318, 1245, 1240, and 930 cm^{-1} [cf. Flett (1951).] The acetate, prepared by the use of pyridine and acetic anhydride (1 hr; 100°) formed plates (from water), m.p. 189° to 190°. [Lesser and Gad (1926) record m.p. 191° to 192°.] [Found: C, 60·4; H, 4·35. Calc. for $C_9H_8O_4$: C, 60·0; H, 4·5%.] $\lambda_{max.}^{EtOH}$ 232 mμ (log ε 4·10).

Further extraction of the ether extract with aqueous sodium carbonate and aqueous sodium hydroxide (10%) gave negligible fractions. A small quantity of a green oil was isolated from the neutral fraction but was not further investigated.

Methanol Extract

The black syrupy concentrate, obtained by removal of solvent *in vacuo*, was hydrolyzed with 7% sulphuric acid at room temperature for 24 hr and separated from a deposit of black insoluble polymeric material (55 g), which was washed with hot water (2 l.). The filtrate and washings were then heated under reflux for 2 hr, the solution stood overnight and extracted with ether (3 × 1 l.). p-Hydroxybenzoic acid (1·96 g), was obtained from the ether extracts by working up as in the previous manner.

The aqueous hydrolysate was re-extracted with butan-1-ol until the extracts were colourless and the gummy concentrate examined for vitexin by paper chromatography. Examination of the remaining aqueous hydrolysate by circular paper chromatography with phenol-water (9:1) gave a single spot identical with that obtained from glucose run as control (aniline hydrogen phthalate spray reagent).

The Bark

Finely ground bark (1·12 kg) of *Vitex lucens* was successively extracted (Soxhlet) with light petroleum (b.p. 50-60), ether and methanol, each extraction for 36 hr.

Light Petroleum Extract

The waxy solid (4·34 g) obtained on removal of solvent was chromatographed in benzene on alumina (Brockmann II) after removal of a green oil (120 mg) by partial purification from glacial acetic acid.

(a) *Fraction 1*: Elution with benzene gave fractions containing a mixture of aliphatic alcohols with m.p. range 74° to 80°. Rechromatography of the solid fractions gave as the principal component, "ceryl" alcohol (0·40 g), crystallized as waxy plates (from ethyl acetate) m.p.

79° to 80·5° (evac. tube.) [Found, for sample dried to constant weight: C, 81·7; H, 13·8%, *M*, (Rast) 398. Calc. for $C_{26}H_{54}O$: C, 81·6; H, 14·2%; *M*, 383.] [Pollard *et al.* (1931) record m.p. 79·3° to 79·6° for "ceryl" alcohol.] The acetate, prepared by the use of pyridine and acetic anhydride (90°; 1 hr) crystallized from methanol-chloroform in fine needles, m.p. 58·5° to 60°. Oxidation of the crude alcohol with chromium trioxide in acetic acid by the method of Pollard *et al.* (1931) gave "cerotic" acid which crystallized from ethyl acetate as fine needles, m.p. 82° to 84°. [Pollard *et al.* (1931) quote m.p. 81° to 82° as the usual melting point for "cerotic" acid.]

(b) *Fraction 2*: Elution with ether and benzene-ether mixtures gave β-sitosterol (48 mg), crystallizing from methanol as colourless needles, m.p. and mixed m.p. 137° to 138°. [Found, for sample dried to constant weight: C, 83·6; H, 12·5. Calc. for $C_{29}H_{50}O$: C, 84·0, H, 12·15%.] The infrared spectrum was identical with that of an authentic sample. The acetate formed plates (from methanol), m.p. and mixed m.p. 127° to 128°.

Methanol Extract

Concentration of the extract, *in vacuo*, gave a black tar (58 g) which was re-extracted successively with hot ethyl acetate and hot butan-1-ol until each extract was almost colourless. The residue was redissolved in methanol, and filtered from black polymeric material (2·1 g). Each of the extracts were dried, the solvents removed, *in vacuo* and the residues examined by paper chromatography (Table 2). The butanol-insoluble residue on hydrolysis by the method of Briggs and Cambie (1958) gave vitexin (100 mg) which crystallized from 60% aqueous acetic acid as rhombic prisms, m.p. and mixed m.p. 262° to 263°. Paper chromatographic investigation (butan-1-ol-pyridine-water; 3:1:1) of the aqueous hydrolysate after neutralization with barium carbonate and concentration over concentrated sulphuric acid gave a single spot identical with that from glucose run as control.

Acknowledgements

Acknowledgement is made for assistance from the Research Grants Committee of the University of New Zealand and the author thanks Professor L. H. Briggs for continued interest in this work.

References

Briggs, L. H.; Cambie, R. C., 1958: The Extractives of *Vitex lucens*—1 *Tetrahedron, 3* : 269.

Evans, W. H.; McGookin, A.; Jurd, L.; Robertson, A.; Williamson, W. R. N., 1957: Vitexin. Part I. *J. chem. Soc.* : 3510.

FLETT, M. ST. C., 1951: The Characteristic Infra-red Frequencies of the Carboxylic Acid Group. *J. chem. Soc.* : 962.

GHOSE, T. P.; KRISHNA, S., 1936: Constituents of the leaves of *Vitex negundo*. *J. Indian Chem. Soc., 13* : 634

GOODWIN, T. W., 1955: in "Modern Methods of Plant Analysis," pp. 272-311. Vol. III, Springer-Verlag. Germany.

JURD, L.; GEISSMAN, T. A.; SEIKEL, M. K., 1957: The Flavonoid Constituents of *Spirodela oligorrhiza*. II. The Flavone Constituents. *Arch. Biochem. Biophys., 67* : 284.

LESSER, R.; GAD, G., 1926: Uber die Acetylierung aromatischer Oxy-carbonsauren. *Ber. dtsch. chem. Ges., 59* : 233.

POLLARD, A.; CHIBNALL, A. C.; PIPER, S. H., 1931: The Wax Constituents of Forage Grasses. I. Cocksfoot and Perennial Ryegrass. *Biochem. J. 25* : 211.

POWER, E. B.; MOORE, C. W., 1910: The Constituents of the Leaves of *Prunus serotina*. *J. chem. Soc., 97* : 1099.

SEIKEL, M. K.; GEISSMAN, T. A., 1957: The Flavonoid Constituents of Barley (*Hordeum vulgare*). I. Saponarin. *Arch. Biochem. Biophys., 71* : 17.

PRELIMINARY FLIGHT RECORDS OF DIPTERA TAKEN WITH A MODIFIED ROTHAMSTED LIGHT TRAP OPERATED AT PAIAKA

By R. A. Cumber, Entomology Division, Department of Scientific and Industrial Research, Palmerston North,
and
R. A. Harrison, Plant Diseases Division, Department of Scientific and Industrial Research, Auckland

(Received for publication, 16 April, 1959)

Summary

Flight records are given for 35 species of Diptera taken with a modified Rothamsted light trap operated for one year at the Phormium Research Station, Paiaka.

Introduction

A modified Rothamsted light trap was constructed and set up at Paiaka in July 1949, during a programme which involved the study of insects associated with *Phormium* areas. This trap was kept in operation for one year, and yielded a great assemblage of insect material. The construction of the trap, and the numbers of insects belonging to the different orders taken during the year have already been indicated, as have the identity and flight records for the majority of the Lepidoptera, Coleoptera, and Hemiptera (Cumber, 1950, 1951, 1952).

Some of the Diptera have now been identified by one of us (R.A.H.). Nearly 80 species were taken, but the identity of many of these cannot be established until the work of revising such families as the Tipulidae, Chironomidae, Ceratopogonidae, and Cecidomyiidae has been carried out. The present paper gives information for 35 species of Diptera. It is hoped that at a later date it will be possible to publish further records.

Acknowledgements

Assistance in the maintenance of the light trap was given by Mr W. R. Boyce, Officer-in-Charge of the Phormium Research Station, and by Mr N. W. Fitzgerald, who also assisted in dealing with material collected during the peak of the flight season.

References

Cumber, R. A., 1950: A Year's Operation of a Modified Rothamsted Light Trap. *N.Z. J. Sci. Tech. B 32 (1)*: 1–8.

———, 1951: Flight Records of Lepidoptera Taken with a Modified Rothamsted Light Trap Operated at Paiaka. *Ibid., B 33 (3)*: 187–90.

———, 1952: Flight Records of Coleoptera and Hemiptera Taken with a Modified Rothamsted Light Trap Operated at Paiaka. *Ibid., B 34 (4)*: 242–44.

	21–31 July	1949 Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	1950 Apr.	May	June	1–20 July	Total
Sub-Order NEMATOCERA														
CULICIDAE														
Culex pervigilans Berg.	1			18			4	40						63
ANISOPIDAE														
Anisopus notatus (Hutt.)	35	10	15	22	24	29	684	22	10	2	20		4	877
BIBIONIDAE														
Philia nigrostigma (Walk.)					40									40
Philia segnis (Hutt.)					11									11
SCATOPSIDAE														
Scatopse nicarbonaria Hutt.					1									1
MYCETOPHILIDAE														
Anomalomyia guttata Hutt.	2	2										20	4	28
Macrocera (near) *scoparia* Marsh							42	6	200					248
Mycetophila filicornis Tonn.	156	77	77	50	16		31				8	180	80	675
Sciara agraria Felt.	78	6	20								600	50	140	894
Sciara zealandica Edw.	57	10	82	407	2	179	675	100	100		3,720	500	20	5,852
Zygomyia (near) trifasciata Tonn.	2	1	1									20		24
SIMULIIDAE														
Austrosimulium australense Sch.								1						1
Sub-Order BRACHYCERA														
STRATIOMYIDAE														
Actina sp. (XD. 58)					1									1
Benhamyia apicalis (White)					1									1
Neoexaireta spinigera (Wied.)								1						1
EMPIDAE														
Hilara sp. (XD. 42)				76	16,227	709	947	12						17,971
DOLICHOPODIDAE														
Chrysosoma mobile Hutt.								10						10
Chrysotus (?) sp. (XD. 66)								1						1

Sub-Order CYCLORRHAPHA														
A. Aschiza														
Lonchopteridae														
Lonchoptera dubia Curran	1,340	43	100	19	168	536	490	552	460	670	800	80	40	5,298
Phoridae														
Megaselia comparabilis Sch.								1						1
Syrphidae														
Melanostoma fasciatum Macq.								180						180
B. Schizophora-Acalypterae														
Agromyzidae														
Cerodontha denticornis (Panz.)								1						1
Sciomyzidae														
Helosciomyza subspinicostata (T. & M.)					2									2
Sapromyzidae														
Poecilohetaerella antennata Harr.	5		1	5	32			50			5			98
Coelopidae														
Chaetocoelopa littoralis (Hutt.)	1		4	22		16								43
Helomyzidae														
Prosopantrum flavifrons (T. & M.)	7	6	6	4	1	2		40						66
Sphaeroceridae														
Leptocera thomasi Harr.	230	1			310	566	535	3,250						4,892
Drosophilidae														
Dropohila buskii Coq.	1													1
Ephydridae														
Hydrellia enderbii (Hutt.)	2						40	44						86
Chloropidae														
Gaurax flavoapicalis (T. & M.)			8											8
C. Schizophora-Calypterae														
Calliphoridae														
Calliphora erythrocephala Meig.					1			5						6
Calliphora hortona Walk.			3	1										4
Tachinidae														
Hyalomyia cockaynei (Mill.)								13						13
Sarcophaga milleri J. & H.							7	56						63
Muscidae														
Hylemyia cana (Maeq.)	2	2						40	100					144

LEAF EXTRACTIVES OF *POMADERRIS ELLIPTICA* LABILL.

By B. F. Cain and R. C. Cambie, Department of Chemistry, University of Auckland

(Received for publication, 20 October 1958)

Summary

Flavonols present in the leaves of *Pomaderris elliptica* as the free compounds and as glycosides have been identified as kaempferol and quercetin by isolation and by paper chromatography. An aliphatic ester isolated as the major fraction by chromatography of a light petroleum extract has been identified as myricyl acetate.

Introduction

Pomaderris elliptica Labill. (New Zealand "Kumerahau") is a shrub species which occurs in the North Island of New Zealand and also in South-East Australia and Tasmania. Following the observation that a crude methanolic extract of the leaves of the yellow-flowered variety contained phenolic constituents, a more detailed examination has resulted in the isolation of the flavonols, kaempferol, and quercetin. To facilitate the isolation, the crude concentrate from an acetone extract was mixed wih Celite and successively re-extracted with light petroleum, benzene, ether, ethyl acetate, and finally methanol.

From the light petroleum extract, an aliphatic ester, isolated as the major fraction by chromatography on alumina, was identified as myricyl acetate after saponification and identification of the products.

No identified products were obtained from the oily concentrate of the benzene extract, by chromatography on alumina, and the absence of phenolic compounds in the extract was shown by paper chromatography.

The ether extract contained two flavonols in small amount, subsequently shown to be kaempferol and quercetin. Kaempferol, the major flavonol present, was isolated as the tetra-acetate after fractionation into sodium carbonate and chromatography on a cellulose column. Kaempferol was again isolated, as the free compound, by similar treatment of the ethyl acetate extract. Kaempferol tetra-acetate, crystallized as a mono-hydrate, showed a characteristic double melting point similar to that reported by Govindachari and co-workers (1954).

The presence of saponins in the methanol extract was suggested by the stable frothing properties shown by the concentrate. Murray (1950) has previously suggested the presence of appreciable amounts of saponins in *Pomaderris* species.

The presence of flavonol glycosides in the methanol extract with spots at or near the solvent front was indicated by paper chromatography, but no satisfactory separation of the glycosides was achieved by chromatography of the phenolic fraction on cellulose columns. After hydrolysis, however, the aglycones were identified by paper chromatography as kaempferol and quercetin. The major aglycone, quercetin, was isolated from a cellulose column and characterized in the same manner as for kaempferol above. Examination of the aqueous hydrolysate by paper chromatography showed the presence of rhamnose, glucose, and xylose.

Paper chromatographic examination of an ether extract of the yellow flowers showed the presence of kaempferol and quercetin, while glycosides which gave the same flavonols after hydrolysis were present in a methanol extract.

EXPERIMENTAL

Microanalyses are by Dr A. D. Campbell, University of Otago, New Zealand. Infrared spectra were measured in KBr discs and ultraviolet spectra were measured for EtOH solutions. Circular paper chromatography of phenolic constituents was carried out on Whatman's No. 1 paper (24 cm) with the following solvent systems: (A) 60% aqueous acetic acid, (B) phenol saturated with water at 22° C. The positions of flavonol spots were shown with ammonia vapour or by spraying with 5% aqueous ferric chloride.

Extraction of the Leaves

The finely milled leaves (air-dried, 1·6 kg) were exhaustively extracted (Soxhlet) with 90% aqueous acetone and the syrupy concentrate intimately mixed with Celite (*c* 500 g). The dried and powdered mass was then successively extracted (Soxhlet) with light petroleum (b.p. 60° to 70°), benzene, ether, ethyl acetate, and methanol, each for 24 hr.

Light Petroleum Extract

The concentrated light petroleum extract was partly separated from chlorophyll by preliminary chromatography on neutralized alumina. The combined solid fractions (1·5 g), eluted with light petroleum, were re-chromatographed on activated alumina (Brockmann II). The major fraction (1·1 g), eluted with benzene, when recrystallized repeatedly from ethyl acetate gave waxy plates of a saturated aliphatic ester, m.p. 73° to 74°. [Found, for sample dried to constant weight: C, 79·4; H, 13·1%; M (Rast), 489, 495. Calc. for $C_{32}H_{64}O_2$: C, 79·9; H, 13·4%; M, 481.] [Sosa (1950) records m.p. 74° to 75° for myricyl acetate.] The ester showed no appreciable absorption in the ultraviolet region. The infrared spectrum showed bands at 1736, 1248 and 1299 cm^{-1}, typical of the carbonyl stretching vibrations of saturated

acetates (Bellamy, 1954). Saponification with 2N methanolic potassium hydroxide and repeated crystallization from ethyl acetate gave myricyl alcohol as colourless plates, m.p. 85·5° to 86·5°. [Found: C, 82·2, 82·2; H, 14·1, 14·0. Calc. for $C_{30}H_{62}O$: C, 82·1; H, 14·2%.] [Chibnall *et al.* (1934) record m.p. 86·5°.] The infrared spectrum showed primary alcoholic bands at 3390, 1364, and 1066 cm^{-1}. The acid from saponification had b.p. 117° to 118° and gave a positive indigo formation spot test for acetic acid (Feigel, 1956). The p-toluidide formed colourless needles m.p. and mixed m.p. 152° to 153°, from aqueous ethanol. Acetylation of myricyl alcohol regenerated the acetate, m.p. and mixed m.p. 73° to 74°.

Ether Extract

The oily concentrate from the ether extract was redissolved in ether and fractionated between aqueous sodium hydrogen carbonate, aqueous sodium carbonate and 10% aqueous sodium hydroxide. Negligible extracts were obtained from the sodium hydrogen carbonate and sodium hydroxide extracts. The solid (820 mg) from the sodium carbonate extract contained flavonols, R_f 0·60 and 0·48 (A); 0·78 and 0·54 (B), and was chromatographed in 60% aqueous acetic acid on a cellulose column (Whatman standard grade). The middle fraction of a single yellow band was collected and the solvent removed *in vacuo*. Acetylation of the residue and crystallization from ethyl acetate-ligroin and then from aqueous methanol gave colourless needles of kaempferol tetra-acetate monohydrate, melting at 112° to 114°, resolidifying above 120°, and remelting at 178° to 180°. [Govindachari (1954) records softening at 120°, melting at 135°, resolidifying above 135°, and remelting at 176°.]

Ethyl Acetate Extract

The concentrate from the ethyl acetate extract was separated from a small amount of flavonol glycosides by ether extraction, and the ether extract worked up as in the above case. Crystallization from 60% acetic acid, of the residue obtained from the middle fraction of a single yellow band from the column, gave yellow needles of kaempferol (165 mg), m.p. and mixed m.p. 277° to 279° (decomp.). [Found: C, 62·5; H, 3·5. Calc. from $C_{15}H_{10}O_6$: C, 62·9; H, 3·5%.] λ max. 267 mμ (log. ϵ 4·23) and 368 mμ (log ϵ 4·32). The infrared spectrum was identical with that of an authentic sample. The tetra-acetate, crystallized as a monohydrate from aqueous methanol, formed colourless needles which showed identical melting behaviour as recorded above. [Found for sample dried at room temperature: C, 58·7; H, 4·0; Ac, 36·9. Calc. for $C_{23}H_{18}O_{10}.H_2O$: C, 58·5; H, 4·3; 4 Ac, 36·4%. Found for sample dried at 100° to constant weight: C, 60·6; H, 4·1, Ac, 38·3. Calc. for $C_{23}H_{18}O_{10}$: C, 60·8; H, 4·0, 4 Ac, 37·9%.]

Methanol Extract

The concentrate from the methanol extract obtained with the use of an antifrothing device was dissolved in butan-1-ol and the extract fractionated in the previous manner. The sodium carbonate extract gave a solid (2·23 g) which contained flavonol glycosides, R_f 0·86 and 0·78 (A); 0·99 and 0·98 (B). The mixture was hydrolysed with 2N hydrochloric acid for 3 hr and the aglycones extracted with ether. Paper chromatography gave flavonol spots, R_f 0·60 and 0·48 (A); 0·78 and 0·54 (B) identical with those obtained from authentic samples of kaempferol and quercetin. After removal of the ether, column chromatography of the solid residue as in the previous manner, gave quercetin (250 mg), which crystallized from 60% aqueous acetic acid as yellow needles, m.p. and mixed m.p. 313° to 314° (decomp.). [Found: C, 59·1; H, 3·45. Calc. for $C_{15}H_{10}O_7$: C, 59·6; H, 3·3%.] $\lambda_{max.}$ 257 mμ (log ε 4·32), 301 mμ (inflection) and 374 mμ (log ε 4·34). The infrared spectrum was identical with that of an authentic sample. The penta-acetate crystallized from ethanol as colourless needles, m.p. and mixed m.p. 193° to 194°.

Examination of the aqueous hydrolysate by paper chromatography using solvent B gave spots, circular R_f 0·50, 0·58, 0·72, identical with those from glucose, xylose, and rhamnose, respectively.

ACKNOWLEDGEMENTS

The authors thank Dr W. E. Hillis, Division of Forest Products, C.S.I.R.O., Melbourne, and Professor T. R. Govindachari, Presidency College, Madras, for samples of authentic kaempferol and one of us (R.C.C.) acknowledges assistance from the Research Grants Committee of the University of New Zealand.

REFERENCES

BELLAMY, L. H., 1954: "The Infrared Spectra of Complex Molecules," pp. 152-64. Methuen and Sons, London.

CHIBNALL, A. C.; PIPER, S. H.; POLLARD, A; WILLIAMS, E. F.; SAHAI, P. M., 1934: The Constitution of the Primary Alcohols, Fatty Acids, and Paraffins present in Plant and Insect Waxes. *Biochem. J., 28* : 2189.

FEIGEL, F., 1956: "Spot Tests in Organic Analysis", p. 342. 5th edit., Elsevier, Amsterdam.

GOVINDACHARI, T. R.; PAI, B. R.; NAGARAJAN, K., 1954: Chemical Examination of *Tylophora asthmatica*. Part I. *J. chem. Soc.* : 2801.

GUIDER, J. M.; SIMPSON, T. H.; THOMAS, D. B., 1955: Anthoxanthins. Part II. Derivatives of Katuranin and Kaempferol. *Ibid.* : 170.

MURRAY, J., 1949: The Contribution by New Zealand Workers to the Chemistry of Plants: Part II. Investigation of the Native Flora. *J. N.Z. Inst. Chem., 13* : 128.

SOSA, A., 1950: Isolation of some Constituents of the Wax from *Arbutus unedo*. *C. R. Acad. Sci., Paris, 230* : 995.

A LEACHING STUDY OF THE BULLER GORGE URANIUM ORE

By R. M. CARR, School of Mines and Metallurgy,
University of Otago

(Received for publication, 7 October 1958)

Summary

A leaching study of the Buller Gorge uranium ore revealed the applicibility of sulphuric acid as a leaching reagent. Sodium carbonate/bicarbonate leaching could be possible at temperatures approaching 100° C. Owing to sampling difficulties the results are an indication only of favourable conditions for acid leaching viz. 200 lb to 300 lb sulphuric acid per ton of ore (50% solids) at 40° to 60° C. for 3 to 6 hours with oxidant. Tests on grain size indicated that coarse grinding only may be sufficient for efficient acid leaching.

INTRODUCTION

The uraniferous horizons in the Hawks Crag Breccia of Nelson and Westland consist of angular fragments of granite, greywacke, sandstone, quartz, and feldspar cemented with calcite (sometimes dolomite and ankerite in addition), and also contain pyrite, iron oxides, carbonaceous material and the uranium mineral.* The latter has been positively identified (Claridge and Reed, 1957) as the hydrous silicate, coffinite $[U(SiO_4)_{1-x}(OH)_{4x}]$, and appears to be the primary ore mineral and the only one of any consequence in the deposit.

Uranium can be extracted from ores by a variety of methods, but the only leaching agents of industrial importance are sulphuric acid and sodium carbonate/bicarbonate solutions. In the presence of an oxidizing agent, sulphuric acid takes uranium into solution as uranyl sulphate ions. The presence of carbonates, sulphides, and oxides in the ore increases acid consumption. Sodium carbonate/bicarbonate solutions also require oxidant and dissolve uranium as uranyl carbonate ions. Sulphides and silica increase alkali consumption.

The investigations on the ore were designed to find the industrial optimum conditions (i.e., conditions producing 90% or greater extraction) for leaching the uranium. But, since in industry the optimum conditions are sometimes not employed, for economic reasons, it was necessary to study each variable so as to be able to predict the effect of limitations on the optimum conditions.

*Whittle, A. W. G., 1957: "Buller Gorge Uranium Province." Report to Rio Tinto Pty. Ltd. The reference is made by courtesy of this organization.

EXPERIMENTAL

Material

Five samples ranging from 0·151% to 0·890% U_3O_8 in composition were collected from outcrops in the area held by Buller Uranium Ltd. at Tiroroa. The samples had undergone some weathering, the degree of weathering varying from sample to sample. Moreover, as the samples were collected during an early stage in the prospecting, they may not be truly representative of Hawks Crag ore in general.

Grinding and Sampling

The ore material was successively reduced in the dry state by means of a laboratory jaw crusher, rolls, and ball mill. Sieve analyses were carried out and the average grain size of the samples for leaching was in the vicinity of 50% minus 200 mesh Tyler. Each of the samples was split into numerous fractions with a Jones Riffle.

Leaching

Leaching tests on 100 g samples were conducted in beakers, the pulp being agitated by glass stirrers. High temperature leaching was effected by a thermostatically controlled hot-plate; water was added at intervals to maintain the pulp density at 50% solids. The oxidants were manganese dioxide for acid leaching and potassium chlorate for alkali leaching. Each leaching operation was conducted for six hours and samples were withdrawn after three hours. The residues were filtered and washed. The final liquors (including washings) were diluted to 250 ml. The residues and liquours were analysed for uranium, and values for ferrous iron, ferric iron, sulphate, titanium, and phosphate in liquors were determined for some of the samples.

Analytical Procedures

Uranium in liquours was determined by measuring the optical density of the uranium thiocyanate colour developed in butyl cellosolve after extraction with methyl isobutyl ketone using aluminium nitrate as the salting-out reagent (Nietzel and Desesa, 1957) A Hilger Uvispek was used for all optical density determinations.

Since feed samples and residues were too low in uranium content for the above method to be used, they were analysed fluorimetrically. After fusion of the solid sample with potassium bisulphate and solution in dilute sulphuric acid, the uranium was extracted with methyl isobutyl ketone. Small aliquots of the ketone were evaporated and the residue fused at 650° C with a potassium carbonate-sodium carbonate-sodium fluoride flux. After cooling, the fluorescence of the fused cakes was measured in a Galvanek-Morrison fluorimeter (Centanni *et al.*, 1956). Since leaching efficiencies were calculated from residue analyses, the 5% to 10% error in the fluorimetric determinations was reduced to 1% to 2% in the efficiency values.

An attempt was made to determine the uranium content of the feed samples radiometrically. The Buller Gorge uranium is not in equilibrium with its daughter decay products. It was found that the degree of non-equilibrium varied from sample to sample, and so the equation of Eicholz (1953) could not be applied. Errors in radiometric assays were as high as 500% and showed no consistent trend.

Values for ferrous iron, ferric iron, and sulphate were carried out by standard methods. Titanium and phosphate were determined using the methods of Shapiro and Brannock (1956).

RESULTS

The best conditions for leaching the uranium from the ore were found by testing the effect of acid concentration, alkali concentration, time, and temperature on each of the five samples. In addition, other variables were tested and all of the results are given in terms of leaching efficiency (i.e., % extraction) and rates of solution

$$\frac{(\text{Feed \% } U_3O_8 - 3 \text{ hrs \% } U_3O_8)}{3}$$

It will be noted that some of the "best conditions" are not industrial optimum conditions.

Extraction Conditions

Acid and alkali leaching was attempted on each sample and 8 to 15 leaching tests were required. In all the tests, sulphuric acid and sodium carbonate/bicarbonate solutions were used at atmospheric pressure, and the amount of oxidant, the grain size, and pulp density were kept constant. Table 1 shows the detailed results of acid leaching tests on Sample A 100 (0·488% U_3O_8).

Since greater than 90% leaching efficiency is economically suitable in industry, the optimum conditions for Sample A 100 are 200 lb acid and 4 lb manganese dioxide per 2,000 lb at 45° to 50° C and 50% solids for 3 to 6 hr.

In Table 2, the results for alkali leaching on Sample A 104 (0·400% U_3O_8) are shown. The best conditions are 80 lb alkali and 40 lb potassium chlorate per 2,000 lb ore at 80° to 85° C and 50% solids for 6 hr.

The best leaching conditions obtained for all of the samples tested are summarized in Table 3.

Uranium Content and Reagent Consumption

The theoretical amount of acid required for total solution of uranium varied from 3 lb/ton of ore for Sample A 108 to 18 lb/ton of ore for Sample H. From Table 3 it is observed that all samples required more than 200 lb acid/ton of ore due to the presence of up to 9% calcium carbonate and 0·3% iron pyrites as well as significant quantities of other soluble iron minerals. However, increasing uranium content invariably resulted in increased rates of uranium solution for both acid and alkali leaching, irrespective of associated reagent consumers.

TABLE 1.

H_2SO_4 lb/ton	100	200			300			350		400		
Initial normality	1·1	2·1			3·1			3·7		4·1		
Pulp density	50	50			50			50		50		
MnO_2 lb/ton	4	4			4			4		4		
Temperature ° C	54	25	47	54	25	47	54	25	47	25	47	54
Leaching efficiency:												
3 hr	9	62	92	92	69	95	94	70	94	76	95	98
6 hr	18	70	95	98	77	98	98	78	98	83	98	99
Diluted liquour composition:												
U_3O_8 g/li.	0·013	1·47	1·60	1·79	1·58	1·61	2·20	1·58	1·60	1·58	1·61	2·21
Fe^{+++} g/li.	0·01	n.d.	n.d.	0·07	n.d.	n.d.	0·07	n.d.	n.d.	n.d.	n.d.	0·22
Fe^{++} g/li.	1·77	n.d.	n.d.	4·24	n.d.	n.d.	5·50	n.d.	n.d.	n.d.	n.d.	5·59
TiO_2 g/li.	0·001	n.d.	n.d.	0·005	n.d.	n.d.	0·003	n.d.	n.d.	n.d.	n.d.	0·005
P_2O_5	0·001	n.d.	n.d.	0·13	n.d.	n.d.	0·36	n.d.	n.d.	n.d.	n.d.	0·36
SO_4'' g/li.	9·1	n.d.	n.d.	24·3	n.d.	n.d.	42·2	n.d.	n.d.	n.d.	n.d.	59·5

TABLE 2.

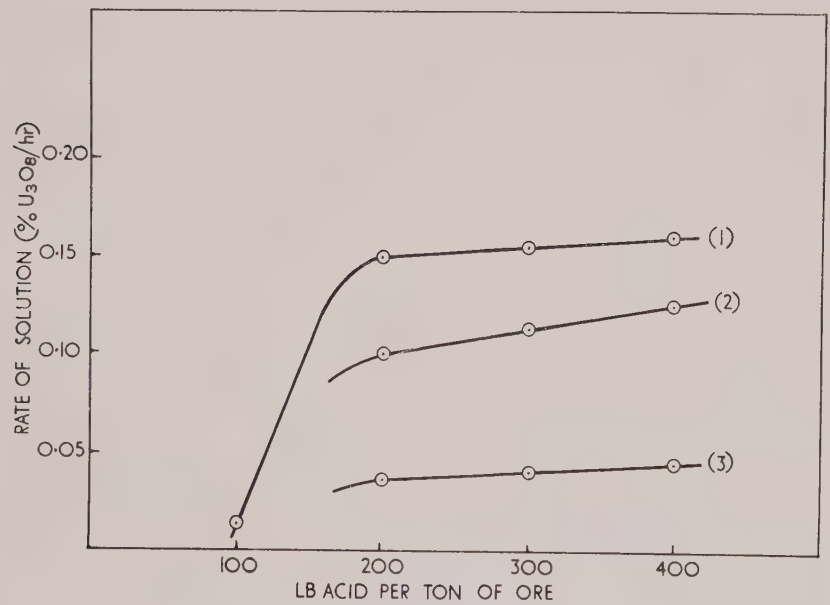
Alkali lb/ton	60			80			100			120		
Pulp density	50			50			50			50		
$KClO_3$ lb/ton	40			40			40			40		
Temperature ° C	53	70	84	53	70	84	53	70	84	53	70	84
Leaching efficiency:												
3 hours	53	64	70	54	70	75	56	69	75	53	70	76
6 hours	69	72	83	75	79	85	73	77	87	71	78	85
Diluted liquour composition:												
U_3O_8 g/li.	1·44	1·13	1·31	1·20	1·14	1·42	1·12	1·13	1·43	1·06	1·25	1·41
P_2O_5	n.d.	n.d.	0·01	n.d.	n.d.	n.d.	n.d.	n.d.	0·03	n.d.	n.d.	n.d.
SO_4 g/li.	n.d.	n.d.	0·07	n.d.	n.d.	n.d.	n.d.	n.d.	0·25	n.d.	n.d.	n.d.

Discrepancies in the values for uranium in liquours arise from varying losses of fines during the transfer of 100 g lots of ore to the leaching vessels.

TABLE 3.
Time = 6 hr; pulp density = 50% solids, amount of oxidant constant.

Sample	% U_3O_8	Acid			Alkali		
		Acid lb/ton	Temp. ° C	Leaching efficiency	Alkali lb/ton	Temp. ° C	Leaching efficiency
A 108	0·151	400	50–60	90	80	80–85	97
A 106	0·255	300	45–50	98	60	60–65	85
A 104	0·400	200	50–60	98	80	80–85	85
A 100	0·488	200	45–50	95	60	80–85	87
H	0·890	300	40	95	120	80–85	83

Figure 1 illustrates the effect of the amount of acid on solution rates for two of the samples tested.



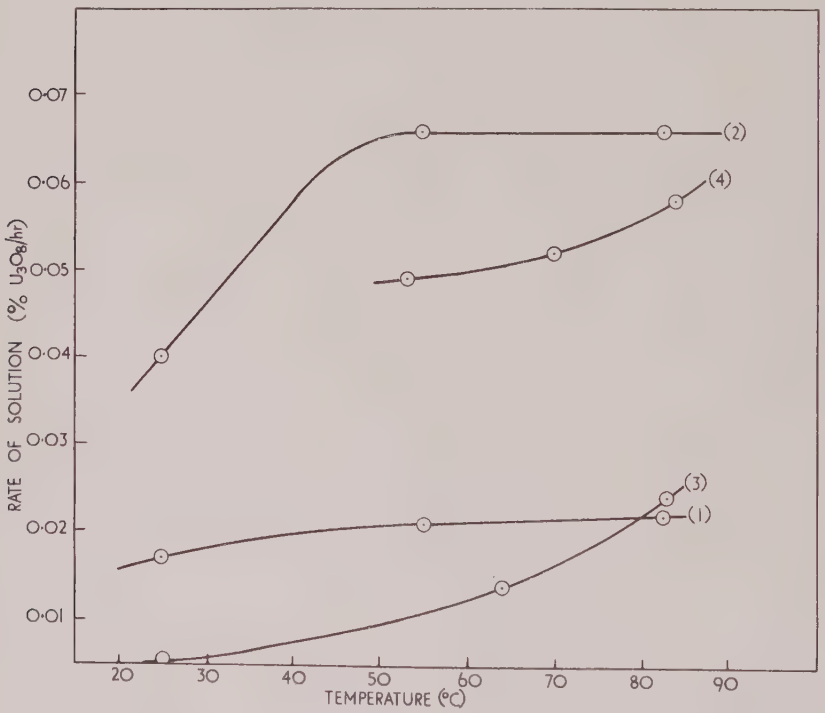
Since the rate increases less above 200 lb acid per ton of ore, it may be concluded that quantities of acid greater than this value represent excess. Similar increasing rates of solution with increasing amounts of reagent were observed for alkali leaching and 60 to 80 lb per ton of ore appears to be the minimum quantity required.

Time

In all cases, except those of extremely inefficient leaching conditions, the rate of solution was high for the 0 to 3 hr period of leaching and markedly low during the second 3 hr. For moderate leaching conditions, the efficiency increased by up to 20% during the second 3 hr, while for good conditions increases were less than 5%.

Temperature

The temperature effect on solution rate indicated a fundamental difference between acid and alkali leaching, as shown by Fig. 2.



(1) SAMPLE A 108 300 lb. ACID
(2) SAMPLE A 104 400 lb. ACID
(3) SAMPLE A 108 80 lb. ALKALI
(4) SAMPLE A 104 100 lb. ALKALI

The increase in the rate of solution for acid leaching (curves (1) and (2)) is less than that for alkali leaching (curves (3) and (4)) with increasing temperature. This indicates a high alkali leaching efficiency for all samples in the temperature range 85° to 95° C.

Oxidant

Tests were conducted with varying amounts of manganese dioxide and potassium chlorate for acid and alkali leaching respectively. Increasing amounts of oxidant (up to 4 lb/MnO_2/ton ore and up to 40 lb $KClO_3$/ton ore) increased the rate of solution of uranium. Without the addition of oxidant, the ore does not contain sufficient ferric iron to facilitate the rapid oxidation and solution of the tetravalent uranium of coffinite.

Pulp Density

Pulp densities of 40, 50, and 60% solids were tested. For acid, maximum leaching efficiencies were obtained at 50% solids. On the other hand, alkali leaching efficiencies increased with increasing pulp densities.

Grain Size

The effect of grain size on leaching efficiencies for both acid and alkali leaching was tested with Sample A 106. Table 4 shows sieve analyses and leaching efficiencies for varying quantities of acid at two temperatures.

TABLE 4.

Tyler screen		Percentages		
		Fine grind	Medium grind	Coarse grind
+ 100		19	42	82
+ 200		26	20	9
— 200		55	38	9
		6 hr leaching efficiencies		
Temp. ° C	lb/ton	Fine grind	Medium grind	Coarse grind
64–66	200	89	91	96
	300	98	98	98
	400	99	99	98
Room	200	44	82	91
	300	54	87	91
	400	78	90	92

Since the uranium values are found in the fine-grained ore cement, the high leaching efficiencies were not expected for the coarse samples. The increasing leaching efficiency with increased grain size at room temperature is probably due to the deleterious effect of flocculation of fines on uranium solution and washing.

Increased grain size caused the expected decreased alkali leaching efficiencies.

CONCLUSIONS

Applicability of the Leaching Reagents

In spite of large quantities of acid consumers in the ore, it appears that sulphuric acid would be a more suitable leaching reagent than sodium carbonate/bicarbonate, from chemical and economic considerations. Alkali leaching may be efficient with 60% solids at temperatures approaching 100° C, but such conditions could result in costly extraction operations. Since acid leaching is regarded as more favourable, the leaching variables are discussed with reference only to the acid process.

Leaching Variables

The results suggest the following optimum values for the leaching variables:

(1) *Amount of acid.*

200 to 300 lb of sulphuric acid per ton of ore is sufficient for excellent recoveries for most of the samples.

(2) *Time*

3 hr leaching time is necessary and sometimes sufficient. The maximum time required is 6 hr.

(3) *Temperature*

Moderate temperatures ranging from 40° C to 60° C are indicated. Increased grain size could lower the optimum temperature required for efficient leaching.

(4) *Oxidant*

4 lb of manganese dioxide per ton of ore is necessary for efficient leaching under the conditions stated above.

(5) *Pulp density*

The acid process is favoured by a pulp density of 50% solids.

(6) *Grain size*

Fine grinding would appear to be unnecessary for acid leaching, since coarse grinds give improved leaching at room temperature. Further investigation is required for a definite grain size to be recommended.

GENERAL

It is evident that, due to variations caused by weathering processes, tests on surface samples are not altogether reliable. Only fresh samples obtained at depth in the ore-body will provide reliable information on leaching characteristics. The above results should, however, provide an indication of the possible leaching behaviour of fresh ore samples.

ACKNOWLEDGEMENTS

The author expresses his thanks to the Council of the University of Otago for granting him the opportunity of doing this work, and to Dr G. J. Williams, of the School of Mines and Metallurgy, who suggested the project. The author was introduced to uranium technology through the kindness of members of the South Australian Mines Research and Development Laboratories, who allowed him to work with them for two months. Thanks are also expressed to Mr T. J. McKee for permission to visit his uranium properties and take samples, and to Mr D. Bullen, who accompanied the author in the field. The cooperation of the Chemistry Department, University of Otago, which made available the Hilger spectrophotometer, chemicals, and apparatus, is acknowledged.

REFERENCES

CENTANNI, F. A.; ROSS, A. M.; DESESA, M. A., 1956: *Anal. Chem. 28*: 1651–7.

CLARIDGE, G. G.; REED, J. J., 1957: *Nature 179*: 546.

EICHOLZ, G. G., 1953: *Canad. J. Res. Physics 31*: 613.

NEITZEL, O. A.; DESESA, M. A., 1957: *Anal. Chem. 29*: 556–9.

SHAPIRO, L.; BRANNOCK, W. W., 1956: *U.S. geol. Surv. Bull. 1036–C.*

THE CONSTITUENTS OF *PHEBALIUM NUDUM* HOOK.

PART 2—ALKALOIDS OF THE WOOD

By R. C. CAMBIE, Department of Chemistry, University of Auckland

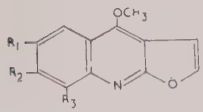
(Received for publication, 23 February 1959)

Summary

The furoquinoline alkaloids, dictamnine, skimmianine, and kokusaginine have been identified in the wood of *Phebalium nudum* Hook. by circular paper chromatography and have been isolated as their picrates. Citral and ellagic acid have also been isolated.

INTRODUCTION

Together with other constituents, the isolation of the furoquinoline alkaloids, dictamnine [I; $R_1 = R_2 = R_3 = H$], γ-fagarine [I; $R_1 = R_2 = H$, $R_3 = OCH_3$], evolitrine [I; $R_1 = R_3 = H$, $R_2 = OCH_3$], skimmianine [I; $R_1 = H$, $R_2 = R_3 = OCH_3$] and kokusaginine [I, $R_3 = H$; $R_1 = R_2 = OCH_3$] from the bark of *Phebalium nudum* Hook. was reported in Part 1 (Briggs and Cambie, 1958).



(I)

Alkaloid fractions have now been isolated from extracts of the wood by fractionation procedures used for the previous examination of the bark constituents. Circular paper chromatography of these fractions and of authentic samples of available furoquinoline alkaloids in five solvent systems ,showed the presence of dictamnine in a light petroleum extract while dictamnine, skimmianine, and kokusaginine were present in both ether and methanol extracts. A further unidentified alkaloid (D) with low R_f values occurred in trace amount only in the methanol extract. Circular R_f values of the furoquinoline alkaloids and of alkaloid D are reported in Table 1. Of the systems used, solvent A gave the most consistent R_f values which could be repeated within $\pm 0{\cdot}02$ and appeared to be little dependent on the time of equilibration of the paper. With solvent B, R_f values varied considerably with the time of equilibration of the paper, longer equilibrating times leading to higher R_f values.

TABLE 1.—R_f Values*.

Compound	Solvent System A	B†	C	D	E
Dictamnine	0·94	0·92	0·88	0·77	0·95
Skimmianine	0·62	0·60	0·79	0·81	0·90
Kokusaginine	0·54	0·52	0·81	0·67	0·91
γ-Fagarine	0·44	0·59	0·87	0·80	0·90
Acronycidine	0·57	0·92	0·93	0·87	0·92
Flindersiamine	0·55	0·93	0·77	0·65	0·87
Alkaloid D	0·29	0·21	0	0	0

A = organic phase of butan-1-ol: 2N HCl (1:1).
B = organic phase of butan-1-ol: 5% HAc (1:1).
C = organic phase of 1% NH_4OH: dioxan: light petroleum (1:1:1)
D = organic phase of 1% NH_4OH: dioxan: light petroleum (2:1:2)
E = organic phase of butan-1-ol: H_2O (1:1).

*R_f values were the average of 4 determinations on Whatman No. 1 paper (24 cm).
†Recorded values were for an equilibration time of 1 hr.

The presence of the alkaloids was confirmed by the isolation, as the picrates, of dictamnine from the light petroleum extract, dictamnine and skimmianine from the ether extract and kokusaginine from the methanol extract. Attempts to isolate alkaloid D from the methanol extract by column chromatography were unsuccessful.

Citral was isolated from the aldehyde fraction of the light petroleum extract but no crystalline phenolic compounds other than ellagic acid were isolated from the wood by methods used in the examination of the bark.

EXPERIMENTAL

Analyses are by A. D. Campbell, University of Otago, New Zealand.

Extraction of the Wood

The finely ground wood (6 kg) was successively extracted (Soxhlet) with light petroleum (b.p. 50° to 60° C), ether and methanol and each extract worked up as for the corresponding extract from the bark (Briggs and Cambie, 1958).

Citral

The aldehyde fraction from the light petroleum extract, isolated via the bisulphite derivative, gave citral (250 mg) b.p. 108° to 112°/10 mm, n_D^{18} 1·4890. The semicarbazone had m.p. 135° to 136°, undepressed by an authentic sample of the same m.p.

Dictamnine

The alkaloid fraction from the light petroleum extract was isolated as the crude picrate. Repeated crystallization from methanol gave, dictamnine picrate (45 mg), m.p. and mixed m.p. 163° to 164°. [Found: C, 50·70; H, 2·88; N, 13·1. Calc. for $C_{12}H_9O_2N$, $C_6H_3O_7N$: C, 50·45; H, 2·85; N, 13·1%.]

Skimmianine

The alkaloid fraction from the ether extract was isolated as the crude picrate. Fractional crystallization from methanol and dioxane gave further dictamnine picrate (21 mg), m.p. and mixed m.p. 163° to 165°, and skimmianine picrate (26 mg), m.p. and mixed m.p. 195° to 196°. [Found: C, 49·42; H, 3·62; N, 11·1. Calc. for $C_{14}H_{13}O_4N$, $C_6H_3O_7N_3$; C, 49·19; H, 3·30; N, 11·5%.]

Kokusaginine

Fractional crystallization of the crude picrate from the alkaloid fraction of the methanol extract gave, as the major product, kokusaginine picrate (14 mg) which crystallized from dioxane as needles, m.p. and mixed m.p. 218°. [Found: C, 48·70; H, 3·15; N, 12·1. Calc. for $C_{14}H_{13}O_4N$, $C_6H_3O_7N_3$: C, 49·19; H, 3·30; N, 11·5%.]

Ellagic Acid

The methanol extract on standing, slowly deposited ellagic acid (320 mg) which, after washing with hot methanol, crystallized from pyridine as pale yellow needles, m.p. > 360°. [Found: C, 55·59; H, 2·22. Calc. for $C_{14}H_6O_8$: C, 55·64; H, 2·00%.] It gave a deep yellow solution with aqueous sodium hydroxide, a blue-black test with ferric chloride and gave positive Greissmeyer and Alvarez tests (cf. King, King, and Ross, 1954). The infrared spectrum was identical with that of an authentic sample crystallized from the same solvent.

ACKNOWLEDGEMENTS

The author gratefully acknowledges assistance from the Research Grants Committee of the University of New Zealand.

REFERENCES

BRIGGS, L. H.; CAMBIE, R. C., 1958: The Constituents of *Phebalium nudum* Hook.—I. The Bark. *Tetrahedron, 2* : 256.

KING, F. E.; KING, T. J.; ROSS, J. M., 1954: The Chemistry of Extractives from Hardwoods. Part XVIII. The Constitution of Arjunolic Acid, a Triterpene from *Terminalia arjuna*. *J. chem. Soc.*: 3995.

WOOD EXTRACTIVES OF *ARISTOTELIA SERRATA*

By R. C. Cambie, Department of Chemistry, University of Auckland

(Received for publication, 16 March 1959)

Summary

β-Sitosterol, β-sitosteryl-D-glucoside and ellagic acid have been isolated from the wood of *Aristotelia serrata.*

Introduction

Aristotelia serrata (New Zealand "Mako-mako") is a small tree which is endemic and common in forests throughout New Zealand. The wood is white and has been used for conversion into charcoal for the manufacture of gunpowder (Laing and Blackwell, 1957). To facilitate isolation of the constituents, the wood was initially extracted with methanol and the concentrate, intimately mixed with Celite, then re-extracted with solvents of increasing polarity.

Light petroleum, benzene, and ether extracts each gave only small residues which were combined and chromatographed on alumina. A crystalline sterol (0·01% yield) isolated from the column was identified as β-sitosterol by comparison of the infrared spectrum with that of an authentic sample and by the preparation of the acetate.

The concentrate from an ethyl acetate extract, on standing, deposited a further sterol (0·1% yield) which gave a positive Molisch carbohydrate test and which was almost insoluble in the usual organic solvents. The compound was identified as β-sitosteryl-D-glucoside by comparison of the infrared spectrum with that recorded by Mā and Schaffer (1953) and by preparation of the tetra-acetate. The identity was confirmed by hydrolysis to β-sitosterol and D-glucose.

The concentrates from both an acetone and a methanol extract, on standing in the presence of acid over a period of weeks, slowly deposited solid material which was sparingly soluble in most organic solvents. The compound (0·7% yield), when crystallized from pyridine was identified as ellagic acid by comparison with an authentic sample and by preparation of derivatives. Standard benzoylation produced a new derivative of ellagic acid, the tribenzoate rather than the expected tetrabenzoate.

No further solid material was obtained by hot acid hydrolysis of the mother liquors of ellagic acid and no sugars were detected when the hydrolysates were examined by paper chromatography.

Experimental

Analyses are by A.D . Campbell, University of Otago, New Zealand. Infrared spectra were measured in KBr discs and ultraviolet spectra were measured in EtOH solutions.

Extraction of Aristotelia serrata Wood

Continuous extraction (Soxhlet) of the finely ground wood (1·3 kg) with methanol for 24 hr and concentration of the extract gave a dark tarry residue which was intimately mixed with Celite. The air-dried solid was re-extracted (Soxhlet), successively with light petroleum, benzene, ether, ethyl acetate, acetone and methanol, each for 24 hr.

β-Sitosterol

The oily residues from the light petroleum, benzene and ether extracts were combined and chromatographed in benzene on activated alumina (P. Spence & Sons, Ltd., grade H). From fractions eluted with ether crystalline material was obtained which gave β-sitosterol (110 mg), plates (from methanol), m.p. and mixed m.p. 136° to 137° C. [Found, for sample dried at 100°: C, 83·7; H, 12·3. Calc. for $C_{29}H_{50}O$: C, 84·0; H, 12·15%. Loss on drying 4·4%. $C_{29}H_{50}O.H_2O$ requires loss 4·2%.] The infrared spectrum was identical with that of an authentic sample. The acetate, needles from methanol, had m.p. and mixed m.p. 126° to 127°. [Found: C, 81·9; H, 11·2. Calc. for $C_{31}H_{52}O_2$: C,81·5; H, 11·5%.]

β-Sitosteryl-D-glucoside

The concentrate from the ethyl acetate extract on standing for 3 months deposited a crystalline solid which was washed well with cold methanol. The residue crystallized from dimethylformamide as colourless rods to give β-sitosteryl-D-glucoside, m.p. 289° to 290° (dependent on the rate of heating); $[\alpha]_D^{22} - 46·8° \pm 0·5°$ (*c* 0·75 in pyridine). Ma and Shaffer record m.p. 290° to 291° and $[\alpha]_D^{21} - 46·9° \pm 1·5°$ (pyridine). A further yield was obtained by concentration of the methanol washings (total yield, 159 mg). [Found: C, 72·1; H, 10·25. Calc. for $C_{35}H_{60}O_6$: C, 72·9; H, 10·5%.] The compound was insoluble in water, alkali, and most organic solvents, and gave positive Liebermann-Burchard and Molisch tests. The ultraviolet spectrum showed no absorption while the infrared spectrum showed close correspondence with that recorded for mulls by Ma and Schaffer. The tetra-acetate, prepared by the use of acetic anhydride and pyridine (2 hr; 100°) formed long glistening needles (from methanol), m.p. 166° to 167°. Ma and Shaffer record m.p. 165° to 165·5°. [Found: C, 69·4; H, 8·9. Calc. for $C_{43}H_{68}O_{10}$: C, 69·3; H, 9·2%.]

Hydrolysis of the compound by the method of Jurd (1956) gave β-sitosterol, m.p. 137° to 138° (identical infrared spectrum), and D-glucose was detected in the hydrolysate by comparative circular paper chromatography (phenol saturated with water at 22°).

Ellagic Acid

The concentrates from the acetone and methanol extracts on standing in the presence of 2N hydrochloric acid at room temperature, each deposited yields of amorphous red material which were washed well

with hot methanol. The residue then crystallized from pyridine to yield pale yellow needles of ellagic acid, m.p. > 360°. A further yield was obtained by concentration of the methanol washings (total yield, 9·0 g). [Found: C, 55·7; H, 2·1. Calc. for $C_{14}H_6O_8$: C, 55·6; H, 2·0.] $\lambda_{max.}$ 256 mμ (log ε 4·64) and 368 mμ (log ε 4·03). The infrared spectrum was identical with that of an authentic sample crystallized from pyridine. When crystallized from (a) dimethylformamide (long bronze needles), or (b) ethylene glycol (yellow needles) ellagic acid retained solvent of crystallization when dried at 100° *in vacuo*. [(a) Found: C, 54·8, 54·9, 54·4; H, 3·7, 3·6, 4·2; N, 5·5, 5·5. Calc. for $C_{14}H_6O_8.C_3H_7ON$: C, 54·4; H, 3·5; N, 3·7% (b) Found: C, 53·3; H, 3·6. Calc. for $C_{14}H_6O_8.C_2H_6O_2$: C, 52·8; H, 3·3%.]

The tetra-acetate, colourless needles from pyridine-acetic anhydride, had m.p. 342° to 343°. [Found: C, 56·2; H, 3·5; Ac, 36·0. Calc. for $C_{22}H_{14}O_{12}$: C, 56·2; H, 3·0; 4 Ac, 36·1%.] The tribenzoate, prepared by the use of benzoyl chloride and pyridine (2 hr; 100°) crystallized from dimethylformamide-ethanol as needles, m.p. 309°. [Found: C, 68·1; H, 3·4; Bz, 51·8. $C_{35}H_{18}O_{11}$ requires C, 68·4; H, 3·0; 3 Bz, 51·3%.] The infrared spectrum showed hydroxyl absorption at 2·87 μ.

The tetramethyl ether, plates (from dimethylformamide), m.p. 346° to 348°, was prepared either with diazomethane in methanol-ether or by prolonged heating of a suspension in acetone with dimethyl sulphate and anhydrous potassium carbonate. King, King, and Ross (1955) record m.p. 343° to 344°.

ACKNOWLEDGEMENTS

The author gratefully acknowledges assistance from the Research Grants Committee of the University of New Zealand and thanks Dr B. F. Cain for preliminary work on the extract.

REFERENCES

JURD, L., 1956: The Sterol and Carbohydrate Constituents of the Walnut (*Juglans regia*). *J. org. Chem.*, *21* : 759.

KING, F. E.; KING, T. J.; ROSS, J. M., 1955: The Chemistry of Extractives from Hardwoods. Part XXIII. The Isolation of a New Triterpene (Terminolic Acid) from *Terminalia ivorensis*. *J. chem. Soc.* : 1333.

LAING, R. M.; BLACKWELL, E. W., 1957: "Plants of New Zealand," 6th edit., Whitcombe & Tombs Ltd., N.Z., p. 258.

MA, R. M.; SCHAFFER, P. S., 1953: β-Sitosteryl D-Glucoside and β-Sitosterol from Commercially Dried Grapefruit Pulp. *Arch. Biochem. Biophys.*, *47* : 419.

SEPARATION AND IDENTIFICATION OF FOOD COLOURS

By ALISON C. COOKE, Dominion Laboratory, Department of Scientific and Industrial Research, Wellington

(Received for publication, 12 March 1959)

Summary

The 17 water-soluble coal-tar food colours permitted in New Zealand were separated and identified by the paper chromatographic method of Thaler and Sommer modified by the use of a second solvent. Rf values in sodium citrate/ammonia and in butanol/ethanol/water are tabulated for 41 food colours, including those authorized in England, and details are given for the identification of the spots.

INTRODUCTION

Many publications have described the separation of food dyes by means of paper chromatography alone or combined with column chromatography, and a wide variety of solvents has been employed (Fouassin, 1952; Tilden, 1952 and 1953; Thaler and Sommer, 1953; Sclar and Freeman, 1955; Anderson *et al.*, 1957). Some of the separation schemes are time-consuming and none includes all of the 17 colours permitted in New Zealand. For example, the comprehensive studies of Fouassin (1952) and Thaler and Sommer (1953), each dealing with about 80 dyes, include only 10 and 8 respectively of these permitted colours.

For the routine examination of foodstuffs for added colour, the rapid method of thaler and Sommer (1953) modified by the use of a second solvent has been used in this laboratory for more than a year with very satisfactory results. Data are here presented for the identification of 41 colouring agents likely to be encountered in foods in New Zealand, including dyes permitted prior to 1956, those permitted under Amendment 11 (1956) of the Food and Drug Regulations, 1946, and those of the United Kingdom recommended list of 1957.

MATERIALS AND METHOD

Reference Dyestuffs

Food grade dyes were supplied by Williams Ltd. (Hounslow), England, and Imperial Chemical Industries (N.Z.) Ltd., and a few by W. J. Bush & Co. Ltd., London.

Two samples of each dye were obtained from different manufacturers and gave identical Rf values in each case. Only one sample each

of the following was available: Yellow RFS, Yellow RY, Violet BNP, Benzyl Violet 4B, Chocolate Brown FB, and Chocolate Brown HT. Secondary spots, sometimes used in the identification of a dye, were recorded in this work only when they occurred in both samples.

Developing Solvents

Solvent 1 was prepared by dissolving 2 g of trisodium citrate dihydrate in 100 ml of 5% w/v ammonia (Thaler and Sommer, 1953). Solvent 2 was composed of n-butanol/95% ethanol/water (1:1:1) (Anderson *et al.*, 1957).

Method

The extraction method was that described by Thaler and Sommer (1953) for the different types of foodstuffs, the colour being isolated by the wool-dyeing process using chemically purified unbleached wool. A minimum quantity of hydrochloric acid was used instead of potassium hydrogen sulphate to acidify the solution before dyeing. The dyed wool was washed thoroughly with hot water and the colour stripped with ammonia. The solution was then evaporated to half its original volume to remove the ammonia, made just acid with hydrochloric acid, and the colour dyed on wool a second time. In this way, salt contamination was kept at a minimum. The dye was again stripped, the solution evaporated almost to dryness, and then spotted in varying amounts on sheets of Whatman No. 1 paper. Reference dyes were spotted alongside or mixed with the unknown dye as internal standards. Two ascending chromatograms were run, one for 2 hours with Solvent 1 and the other for 7 hours with Solvent 2. The dry chromatograms obtained with Solvent 1 were examined for fluorescence under ultra-violet light, and then 10% sodium hydroxide and concentrated hydrochloric acid were applied with capillaries to the coloured spots as described by Thaler and Sommer (1953).

RESULTS AND DISCUSSIONS

Although the Rf value of a dye in Solvent 1, together with its colour, fluorescence, and reaction to spot tests, as used by Thaler and Sommer (1953), was often sufficient to identify the dye, it was not found conclusive in every case. By the use of Solvent 2, it was possible to confirm the result and also to separate many dye mixtures which were not resolved by Solvent 1. More compact and more brightly coloured spots were obtained with Solvent 2, and the triphenylmethane dyes and Indigo Carmine retained their colour in this solvent. These dyes were decolorized by Solvent 1, and the original colour, especially with Indigo Carmine and Acid Green G, did not always return on drying the chromatogram.

Rf values in both solvents for the 41 dyes are listed in Table 1, together with data for their further identification. All the dyes are acidic, with the exception of Rhodamine B, a basic dye.

TABLE 1.—Data for the Identification of Food Dyes.

Ascending chromatography at 20° C on Whatman No. 1 paper (paper not equilibrated).
Solvent 1: 2% sodium citrate in 5% ammonia; run for 2 hours; solvent front 24 cm.
Solvent 2: Butanol/ethanol/water (1:1:1); run for 7 hours; solvent front 18 cm.

C.I. No.*	Dye	Rf value Solvent 1	Rf value Solvent 2	Colour on chromatogram with Solvent 1		Fluorescence	Spot tests	
				Wet	Dry		10% NaOH	conc. HCl
	YELLOW							
639	Yellow 2G	0·85	0·74	greenish yellow	greenish yellow		no change	no change
640	Tartrazine‡	0·78	0·40	yellow	yellow		no change	no change
13011†	Yellow RFS	0·63	0·58	yellow	yellow	yellow	no change	bluish red
13011†	Yellow RFS (dyed)	0·35	0·75 (0·58)	yellow	yellow		no change	bluish red
16	Acid Yellow G	0·62 (0·37)	0·57 (0·76)	greenish yellow	greenish yellow		no change	red
10	Naphthol Yellow S	0·48	0·71	greenish yellow	greenish yellow		no change	colourless
14330†	Yellow RY	0·46 (0·76)	0·36 (0·49)	yellowish brown	yellowish brown		pink	no change
	ORANGE							
27	Orange G	0·77	0·65	orange	orange		pale violet	no change
15985†	Sunset Yellow FCF‡	0·58	0·59	orange	orange		browner	no change
26	Croceine Orange‡§	0·46 (0·54)	0·83 (0·60)	orange	orange		pale yellow	reddish orange
151	Orange II	0·35	0·80	orange	orange		browner	red
150	Orange I	0·31	0·80	red	red		reddish violet	bluish violet
	RED							
692	Acid Magenta II	0·97	0·55 (0·70)	colourless	pinkish violet		pale green, then colourless	pale green, then colourless
185	Ponceau 4R‡	0·71	0·47	red	red		green, then brownish yellow	no change
31	Red 2G	0·62 (0·22)	0·48	brownish red	bluish red		yellow	no change
184	Amaranth‡	0·53 (0·39)	0·44 (0·67)	violet-red	violet-red		pale brown	no change
749	Rhodamine B	0·10–0·45	0·96	bluish pink	bluish pink	bright orange	no change	pale green
57	Red 6B‡	0·44	0·41	reddish violet	reddish violet	dull bluish red	orange	no change
14700†	Ponceau SX‡	0·44	0·64	orange	red	orange-red	orange	no change
182	Fast Red E	0·41	0·67	red	red		pale brown	no change
79	Ponceau 2R	0·28 (0–0·47)	0·54	red	red		pale yellowish brown	no change
30	Red 10B	0·27	0·46	violet-red	violet-red	dull bluish red	browner	reddish orange

179	Carmoisine‡	0·27	0·68	red	bluish red	dull red (solvent 2 only)	red	red, with red fluorescence
80	Ponceau 3R	0·24 (0·05–0·47)	0·54	red	red	dull-orange-red	pale yellowish brown	no change
768	Eosine	0·13 (0·20)	0·77	yellowish pink	yellowish pink	bright greenish yellow	no change	yellow
773	Erythrosine	0·05 (0·13)	0·78	bluish pink	bluish pink	orange	no change	yellow
225	Red FB‡	0	0 0·47	bluish red	bluish red	bluish red	mauve	no change
448	Benzopurpurine	0	0–0·38	red	red	dull orange-red	no change	blue
	BLUE AND GREEN							
737	Green S‡	0·89	0·74	blue	greenish blue		blue	yellowish orange
670	Light Green SF	0·88	0·70	colourless	green	green	colourless	yellowish orange
671	Brilliant Blue FCF	0·88	0·72	greenish blue	greenish blue		no change	yellow
672	Blue VRS‡	0·80	0·79	greenish blue	greenish blue		no change	yellow
666	Acid Green G	0·70	0·83	colourless	colourless or green		colourless	yellowish orange
1180	Indigo Carmine‡	0·21	0·42	colourless	colourless or pale blue		colourless	no change
	VIOLET							
–	Violet BNP	0·69	0·72	colourless	violet		colourless	yellow then colourless
697	Benzyl Violet 4B	0·53	0·82	colourless	violet		colourless	yellow then colourless
698	Violet 5BN‡	0·53	0·82	colourless	violet		colourless	yellow then colourless
	BROWN							
–	Brown FK‡	0·03	0·58	orange-brown	orange-brown		no change	no change
		0·21	0·46	yellow-brown	yellow-brown			pink
–	Chocolate Brown FB‡	0·02 (0–1·0)	0–0·50	pinkish brown	pinkish brown		no change	no change
20285†	Chocolate Brown HT‡	0·02 (0–1·0)	0–0·50	pinkish brown	pinkish brown		mauve	no change
	BLACK							
865	Nigrosine	0–1·0	0–0·50	bluish grey	bluish grey		no change	dull blue
28440*	Brilliant Black BN	0·1–0·34 (0·02)	0 0·30	black-blue	black-blue		no change	fleeting greenish blue

*Rowe's "Colour Index" (1924) Number. †"Colour Index" (1956) Number; no number allotted in 1924.
‡permitted in New Zealand under Amendment 11 (1956) of the Food and Drug Regulations, 1946. §permitted in sausage skins only.
Rf values in parentheses refer to secondary spots.

When a solution containing all 17 of the permitted colours was chromatographed with Solvent 1, 12 coloured zones were distinguishable. These were, in order of decreasing Rf value: Acid Magenta II, Green S, Blue VRS, Tartrazine, Ponceau 4R, Sunset Yellow, Amaranth and Violet 5BN together, then 3 dyes, Croceine Orange, Ponceau SX, and Red 6B as one red zone, Carmoisine, Brown FK, which forms two spots, one yellow-brown and one orange-brown, and Red FB at the origin. Chocolate Brown FB and Chocolate Brown HT, both of which are permitted under the term "Chocolate Brown" of the Regulations, formed a pinkish-brown streak between the two spots of Brown FK. These two chocolate browns have similar Rf values in both solvents, but Chocolate Brown HT may be distinguished by the mauve colour formed with sodium hydroxide. Croceine Orange, Ponceau SX, and Red 6B separate in Solvent 2, the Rf values being 0·83, 0·64, and 0·41 respectively. Amaranth and Violet 5BN also separate in Solvent 2, having Rf values of 0·44 and 0·82 respectively.

The data given in Table 1 for the 41 dyes show that, with few exceptions, separations not achieved by Solvent 1 are possible with Solvent 2. Ponceau SX and Fast Red E separate partially in Solvent 1, forming a red-orange and a bluer red zone. Ponceau SX is recognized by the orange colour formed with alkalis and by its orange-red fluorescence. A clear separation of these two reds is obtained in one hour with the solvent butanol saturated with ammonia, when Fast Red E travels further. Acid Yellow G and Sunset Yellow separate partially in Solvent 1, forming a yellow and an orange zone, the former being distinguished by the red colour with hydrochloric acid. Yellow RFS and Acid Yellow G have similar Rf values in both solvents, but a separation is possible in one hour with normal hydrochloric acid/ethanol (9:1), which also separates them from Sunset Yellow. The chromatogram obtained with a mixture of these three colours shows a blue-red spot (Yellow RFS), an orange-red spot (Acid Yellow G), and an orange spot (Sunset Yellow) (approximate Rf values 0·75, 0·62, 0·32 respectively). For the two special separations mentioned above, short chromatograms were run in wide test tubes.

The permitted colour Green S is distinguished from those of close Rf value, Light Green SF and Brilliant Blue, by the dark blue colour formed in Solvent 1 or when the dry chromatogram is held over ammonia. Under these conditions, Light Green SF is immediately decolorized and Brilliant Blue remains unchanged. Benzyl Violet 4B and Violet 5BN, which have a closely related chemical structure, were not resolved, but were separated from Violet BNP by both Solvents 1 and 2.

Each of the 41 dyes was chromatographed before and after dyeing on wool, and the same Rf values were obtained for the main spot, except in the case of Yellow RFS, which was changed by the dyeing process. Hence two sets of values are quoted for this dye in Table 1. Minor changes occurred with some colours on dyeing, resulting in loss of secondary spots or the formation of new secondary spots, fluorescent spots, or streaks on the chromatogram. The first attempts to apply this method to colours recovered after dyeing resulted

in decreased Rf values and V-shaped spots, which were found to be caused by impurities in the several brands of white wool yarn tried, despite their careful purification as described in the original method. This was overcome by using unbleached pure wool blanket fabric purified in the same way, as no suitable yarn was available. A similar interference has recently been reported by Thaler and Mühlberger (1958). Increase in Rf values with increase in concentration of some of the reference dye solutions, notably Rhodamine B and Brilliant Black BN, made it necessary to spot several concentrations of an unknown dye solution. Figures quoted in Table 1 were obtained with 30 μg of the dye. The use of internal standards enables a correction to be made should impurities cause a depression in Rf values.

The method has been applied to beverages, jams, tinned and dried fruit, fruit sauces, essences, wines, and confectionery. The colouring matter in saveloy skins was also identified after preliminary extraction with 5% ammonia in 70% alcohol, followed by dyeing.

Although Rf values in one or other of the two solvents have been published previously for a number of the dyes studied, they have been included here for the sake of completeness. Rf values were comparable with, but slightly lower than, those obtained by Thaler and Sommer (1953) using a different paper. Although some of the values were in agreement, others differed considerably from those reported by Anderson *et al.* (1957), who employed a butanol/hydrochloric acid extraction.

Acknowledgements

The author wishes to thank Imperial Chemical Industries (N.Z.) Ltd. and Williams Ltd. (Hounslow), England, for supplying samples of the many dyestuffs.

References

ANDERSON, J. R. A.; LOCK, L. C.; MARTIN, E. C., 1957: *Aust. J. Appl. Sci., 8*: 112.

ANON., 1956: "Colour Index"; 2nd ed. Society of Dyers and Colourists, Bradford, and American Assoc. Textile Chemists and Colourists, Mass.

FOUASSIN, A., 1952: *Rev. Ferment., 7*: 195.

ROWE, F. M., 1924: "Colour Index". Society of Dyers and Colourists, Bradford.

SCLAR, R. N.; FREEMAN, K. A., 1955: *J. Ass. off. agric. Chem. Wash., 38*: 796.

THALER, H.; MUHLBERGER, F. H., 1958: *Z. Lebensmitt Untersuch., 108*: 17.

THALER, H.; SOMMER, G., 1953: *Z. Lebensmitt Untersuch., 97*: 345 and 441. *Chem. Abstr., 48*: 2376h and 4714i, 1954.

TILDEN, D. H., 1953: *J. Ass. off. agric. Chem. Wash., 36*: 802.

———, 1952: *J. Ass. off. agric. Chem. Wash., 35*: 423.

DIPHENYLAMINE RESIDUES ON APPLES

EFFECT OF DIFFERENT DIPHENYLAMINE TREATMENTS

By HELEN E. HARVEY and P. J. CLARK, Dominion Laboratory, Department of Scientific and Industrial Research, Wellington

(Received for publication, 25 March 1959)

Summary

Apples treated with diphenylamine in various ways were examined for the uptake of diphenylamine. The amount present depended on the treatment, but in no instance did it exceed 8 p.p.m. Ninety per cent. or more of the diphenylamine was in the outer 2 to 4 mm of the fruit.

INTRODUCTION

During the three years since Smock (1955) showed that diphenylamine is an effective agent for the control of apple scald, the authors have studied the effect on residues of four different methods of applying diphenylamine. Samples of harvested apples were (a) wrapped in diphenylamine impregnated wraps, (b) dipped in suspensions of diphenylamine, (c) sprayed in the case, or (d) apples were sprayed on the tree. The suspensions used for dipping contained 1,000 p.p.m. or 2,000 p.p.m. of "Analar" diphenylamine in 50% ethanol. Those used for spraying were made by preparing 2% of commercial flake diphenylamine in isopropanol, and adding sufficient to water containing 0·05% Tween 20 (a surfactant), to give 500 p.p.m. diphenylamine or 1,000 p.p.m. diphenylamine.

EXPERIMENTAL

The methods of analysis have been described (Harvey, 1958).

The distribution of diphenylamine in treated apples was first studied by determining the amounts present on the surface, in the peelings, and in the pulp of apples. The diphenylamine was removed from the surface of the skin by shaking four or five apples (600 to 750 g) for 5 min. with two successive 70 ml portions of petroleum ether (b.p. 40° to 60° C). The two extracts were filtered, combined, and diluted to a known volume. The apples were then peeled to a depth of 2 to 4 mm and the peelings were extracted. Aliquots of the solutions were taken and the diphenylamine was determined by the method used previously for peelings (Harvey, 1958). Segments were then cut from the peeled

apples and the diphenylamine present in the pulp was determined. In a second series of determinations, the removal of the surface diphenylamine was omitted, and the peelings and the pulp were analysed. Opposite quarters of 7 to 10 apples were peeled to a depth of 2 to 4 mm and the peelings were extracted. Segments were then cut from the same quarters for the pulp analyses.

The results, expressed as parts per million of the total weight of the fruit have been corrected for recoveries of 94% and 86% from the peelings and the pulp respectively (Harvey, 1958).

The results of residue determinations on the pulp, peelings, and surface are given in Table 1, and those on pulp and on peelings in Table 2.

TABLE 1.—Distribution of Diphenylamine Residues on Granny Smith Apples First Series—Content of Pulp, Peelings, and Surface.

Treatment	Concentration of diphenylamine	Time in cool storage (days)	Diphenylamine			
			Pulp (p.p.m.)	Peelings (p.p.m.)	Surface	
					p.p.m.	% of total
Wrapped	1 mg/wrap	210	0·19	0·30	1·9	79
Wrapped	1 mg/wrap	203	0·10	0·21	1·5	83
*Sprayed in the case	1,000 p.p.m.	158	0·06	0·07	0·95	88
†Sprayed in the case	1,000 p.p.m.	158	0·14	0·16	1·5	83
†Sprayed in the case	1,000 p.p.m.	158	0·14	0·15	1·2	80

*Fruit from top of case †Fruit from bottom of case

Table 3 shows the results of residue determinations on Granny Smith apples wrapped in diphenylamine impregnated wraps, and Table 4, residues on several varieties of apples that had been dipped in diphenylamine solutions. Tables 5 and 6 show residues on Granny Smith apples sprayed in the case and on the tree respectively.

DISCUSSION

Except in one instance (Table 5), in which no replicate was available, the apparent diphenylamine content of untreated apples was negligible.

The distribution of diphenylamine in the treated apples as shown in Tables 1 and 2 is of interest. Bruce *et al.* (1958) analysed apples that had been dipped in solutions of diphenylamine at concentrations of 2,000 p.p.m. or 3,000 p.p.m. and cool stored for 112 or 125 days. They found that, for the two varieties studied, Arkansas and Rome Beauty, about half of the total diphenylamine residue of 3·7 to 4·1 p.p.m. was present on the surface. The results presented in this paper

TABLE 2.—Distribution of Diphenylamine Residues on Apples
Second Series—Content of Pulp and Peelings.

Treatment	Concentration of diphenylamine	Variety	Time in cool storage (days)	Diphenylamine		
				Pulp (p.p.m.)	Peelings	
					p.p.m.	% of total
Wrapped	1 mg/wrap	Granny Smith	200	0·17	1·75	91
Wrapped	1 mg/wrap	Granny Smith	207	0·11	1·95	95
Wrapped	1 mg/wrap	Granny Smith	210	0·21	2·5	92
Dipped	1,000 p.p.m.	Statesman	148	0·04	1·85	98
Dipped	2,000 p.p.m.	Statesman	148	0·10	3·4	97
Dipped	1,000 p.p.m.	Dougherty	183	0·05	1·4	96
Dipped	1,000 p.p.m.	Frimley B'ty	133	0·08	0·70	90
*Sprayed in case	1,000 p.p.m.	Granny Smith	‡	0·32	5·8	95
†Sprayed in case	1,000 p.p.m.	Granny Smith	‡	0·37	6·6	95
†Sprayed in case	1,000 p.p.m.	Granny Smith	‡	0·52	7·7	94
Sprayed on tree	500 p.p.m.	Granny Smith	‡	0·01	0·57	98
Sprayed on tree	1,000 p.p.m.	Granny Smith	‡	0·01	0·64	98
Sprayed on tree	1,000 p.p.m.	Granny Smith	‡	0·01	0·50	98

*Fruit from top of case †Fruit from bottom of case
‡Anlysed 7 days after treatment

indicate that this does not apply generally. Thus, with Granny Smith apples that had been wrapped in diphenylamine-impregnated wraps or sprayed in the case and cool stored for 210 to 158 days (Table 1), 79% to 88% of the total diphenylamine was removed by solvents from the surface, and an average additional 10% remained in the outer portion of the apple. The data in Table 2 supported this finding and showed that 90% to 98% of the total diphenylamine was present in the outer 2 to 4 mm of the fruit, and that the percentage did not appear to depend on the variety of apple or on the method of application of the diphenylamine.

Further pulp analyses in Tables 3 and 5 add support to the view that, as the major part of the diphenylamine residue is in the outer 2 to 4 mm of the apple, analysis of the pulp is unnecessary. This can result in a considerable saving in time in residue determinations, and makes possible the use of the simpler method reported for peelings (Harvey, 1958).

With Granny Smith apples in diphenylamine wraps, the residues in the 1957 season (Table 3) gave an average value for 6 pickings of 1·0 p.p.m. (range 0·5 to 1·85 p.p.m.), whereas in the following year the average residue for 16 pickings was 2·05 p.p.m. (range 1·35 to 2·55 p.p.m.).

TABLE 3.—Diphenylamine Residues on Granny Smith Apples Wrapped in Diphenylamine Wraps

Year	Concentration of diphenylamine mg/wrap	Time in cool storage (days)	District	Diphenylamine (p.p.m.)					
				Peelings			Pulp		
				Replicate			Replicate		
				A	B	Mean	A	B	Mean
1957	Nil	155	Nelson	<0·01					
1957	1	139	Nelson	0·80	0·90	0·85			
1957	1	150	Nelson	0·80	0·90	1·85			
1957	1	138	Hastgs.	2·0	1·7	0·85	0·10	0·10	0·10
1957	1	162	Hastgs.	1·4	1·3	1·35	0·07	0·06	0·07
1957	1	138	Auckld.	0·60	0·60	0·60			
1957	1	133	Auckld.	0·50	0·50	0·50			
1958	Nil	147	Nelson	<0·01	0·01	<0·01			
1958	Nil	210	Hastgs.	<0·01	0·02	0·01	<0·01		
1958	Nil	175	Hastgs.	<0·01	0·01	<0·01			
1958	Nil	147	Auckld.	<0·01	<0·01	<0·01			
1958	1	147	Nelson	2·5	2·1	2·3			
1958	1	147	Nelson	1·9	1·9	1·9			
1958	1	172	Nelson	1·85	2·15	2·0			
1958	1	203	Nelson	2·3	2·2	2·25	0·10		
1958	1	148	Hastgs.	2·4	2·7	2·55			
1958	1	175	Hastgs.	2·55	2·35	2·45			
1958	1	210	Hastgs.	2·4	2·6	2·5	0·19		
1958	1	204	Hastgs.	1·6	1·6	1·6			
1958	1	147	Hastgs.	2·1	2·1	2·1			
1958	1	147	Hastgs.	2·3	2·25	2·3			
1958	1	207	Hastgs.	1·9	2·0	1·95	0·11		
1958	1	200	Hastgs.	1·75	1·75	1·75	0·17		
1958	1	119	Auckld.	2·4	2·6	2·5			
1958	1	120	Auckld.	1·35	1·35	1·35			
1958	1	147	Auckld.	1·65	1·7	1·7			
1958	1	147	Auckld.	1·4	1·6	1·5			

The diphenylamine residues on apples dipped in a solution of diphenylamine (Table 4) suggest that differences in varieties may affect the amount of residue since for identical treatment at 1,000 p.p.m. there is a considerable range of residues (0·10 to 1·85 p.p.m.) over the different varieties. Three varieties that had been treated at 1,000 p.p.m. were also treated at 2,000 p.p.m., and the amount of residue followed the same order at each concentration. Granny Smith contained the smallest amounts, Red Statesman slightly more, and Statesman considerably more still.

TABLE 4.—Diphenylamine Residues on Apples After Dipping in Solutions of Diphenylamine

Concentration of diphenylamine (p.p.m.)	Variety	Time in cool storage (days)	Diphenylamine in peelings (p.p.m.)		
			Replicate		
			A	B	Mean
Nil	Ballarat	87	<0·01		
Nil	Granny Smith	155	<0·01		
Nil	Red Statesman	162	<0·01		
Nil	Delicious	223	0·02		
Nil	Frimley Beauty	133	0·02		
Nil	Rome Beauty	84	<0·01		
Nil	Dougherty	183	<0·01		
Nil	Statesman	148	<0·01		
1,000	Ballarat	87	0·10	0·10	0·10
1,000	Granny Smith	155	0·40	0·20	0·30
1,000	Red Statesman	162	0·40	0·40	0·40
1,000	Delicious	223	0·50	0·40	0·45
1,000	Frimley Beauty	133	0·80	0·60	0·70
1,000	Rome Beauty	84	0·80	0·90	0·85
1,000	Dougherty	183	1·3	1·5	1·4
1,000	Statesman	148	1·8	1·9	1·85
2,000	Granny Smith	155	0·90	1·0	0·95
2,000	Red Statesman	162	1·1	1·2	1·15
2,000	Sturmer	217	1·3	1·3	1·3
2,000	Statesman	148	3·5	3·2	3·35

The residues on Granny Smith apples sprayed in the case at a concentration of 1,000 p.p.m. were higher than for any of the other methods of treatment, but in no instance did the amount exceed 8 p.p.m. (Table 5). Cool storage for 158 days of two of these samples reduced the residues from more than 6 p.p.m. to less than 2 p.p.m.

The residues on Granny Smith apples sprayed on the tree at either of two concentrations (500 p.p.m. and 1,000 p.p.m.) and harvested on the day of treatment or 3 days later were, with one exception, less than 1 p.p.m. When there was a delay of 3 days between spraying and harvesting, the residue figures dropped to about half (Table 6).

The results reported here show that when apples were treated by a wet process, the immediate residues were as high as 7 to 8 p.p.m., but that after storage periods of 3 to 7 months the residues were not greater than 3 p.p.m. A statistical treatment of the results after storage indicates that the chances of obtaining more than 3 p.p.m. by any of the methods used are remote.

TABLE 5.—Diphenylamine Residues on Granny Smith Apples Sprayed with Diphenylamine in the Case

Concentration of diphenylamine (p.p.m.)	Position in case	Diphenylamine (p.p.m)					
		Peelings			Pulp		
		Replicate			Replicate		
		A	B	Mean	A	B	Mean
Nil		<0·01	<0·01	<0·01	0·02		
1,000	Top	3·3	2·6	2·95	0·08		
1,000	Bottom	3·9	4·0	3·95	0·02		
Nil		0·05			<0·01		
1,000	Top	6·0	5·8	5·9	0·23	0·32	0·28
1,000	Bottom	5·3	6·9	6·1	0·22	0·25	0·24
Nil		0·12			<0·01		
1,000	Top	6·3	6·6	6·45	0·28	0·37	0·33
1,000	Bottom	5·5	7·7	6·6	0·52	0·52	0·52
*1,000	Top	1·2	1·4	1·3	0·12		
*1,000	Bottom	1·8	1·6	1·7	0·11	0·10	0·11
Nil		0·01	0·05	0·03	<0·01		
1,000	Top	3·9	4·0	3·95	0·30		
1,000	Bottom	7·1	6·2	6·65	0·51		

The fruit was grown in four orchards in Hastings, harvested and sprayed on the same day, and analysed 7 days later. Treatment marked * was analysed after 158 days in cool storage.

TABLE 6.—Diphenylamine Residues on Granny Smith Apples Sprayed with Diphenylamine on the Tree

Concentration of diphenylamine (p.p.m.)	Period between spraying and harvest (days)	Diphenylamine in peelings (p.p.m.)					
		Replicate					
		A	B	C	D	E	Mean
Nil		0·010		0·015	0·015	0·015	0·014
500	0	0·83	0·57	0·45	0·61	0·42	0·58
500	3	0·38	0·25	0·30	0·19	0·23	0·27
1,000	0	0·88	0·64	0·50	0·50	1·1	0·72
1,000	3	0·33	0·34	0·28	0·28	0·79	0·40

The apples were grown in one orchard in Hastings and were analysed 7 days after harvesting.

The mean diphenylamine content of the pulp from six of the samples in Table 6 was 0·01 p.p.m.

ACKNOWLEDGEMENTS

The authors thank Mr J. D. Atkinson, Director of Fruit Research Division, D.S.I.R., Auckland, and Mr C. S. Padfield, Fruit Research Division, D.S.I.R., Havelock North, for supplying the treated apples.

REFERENCES

BRUCE, R. B.; HOWARD, J. W.; ZINK, J. B., 1958: Determination of Diphenylamine Residues on Applies. *J. Agric. & Food Chem., 6*: 597–600.

HARVEY, H. E., 1958: Determination of Diphenylamine Residues on Apples. *N.Z. J. Sci., 1*: 378–82.

SMOCK, R. M., 1955: A New Method of Scald Control. *Amer. Fruit Gr. 75*: 20.

A NOTE ON THE ACETONE-SOLUBLE LIPIDS OF FORAGE GRASSES AND CLOVERS

By R. O. Weenink, Fats Research Laboratory, Department of Scientific and Industrial Research, Wellington

(Received for publication, 29 May 1959)

For some years, investigations on the nature of the lipids of forage grasses and clovers have been in progress in the Fats Research Laboratory (*cf.* Shorland, 1944, 1953). It has been assumed that the chlorophyll-free lipid fraction soluble in acetone at room temperature consisted of triglycerides along with unsaponifiable matter. However, the yield of fatty acids following saponification has usually amounted to only 60 to 70% of that required for a pure triglyceride, after allowing for the presence of unsaponifiable matter.

Recent investigations in this laboratory have shown that the acetone-soluble neutral lipids of clover and forage grasses consist of about 60% of galactosyl glycerol esters of linolenic acid. As an example of the techniques used to demonstrate the nature of the acetone-soluble lipids the experiments with red clover (Trifolium pratense) leaves are described.

The acetone-soluble lipids comprising 5·1% of the dry matter were fractionated on a silicic acid column (Barron and Hanahan, 1958). The fraction eluted with 10% methanol in ether and which contained 85% of the total acetone-soluble lipids had the following composition (% weight): P, 0·08; N, 0·12; unsaponifiable matter 2·2; fatty acids (80% linolenic, Brice *et al.*, 1952), 58·7; carbohydrates as galactose (Bailey, 1958), 34·6 and glycerol (Lambert and Neish, 1950), 17·9. The galactose was identified by chromatography of the acid hydrolysates (Jermyn and Isherwood, 1949).

The theoretical values for 1 molecule each of glycerol, galactose, and fatty acid are (weight %) 17·9, 35·0, and 54·0 respectively. As the carbohydrate moiety of the lipid is non-reducing to Fehlings solution the galactose must be combined with glycerol in position 1 of galactose.

These data are consistent with the structure of galactosyl 1 glycerol linolenate.

REFERENCES

BAILEY, R. W., 1958: *Biochem. J. 68* : 669.

BARRON, E. J.; HANAHAN, D. J., 1958: *J. Biol. Chem. 231* : 493.

BRICE, B. A.; SWAIN, M. L.; HERB, S. F.; NICHOLS, JR. P. L.; RIEMENSCHNEIDER, R. W., 1952: *J. Amer. Oil Chem. Soc. 29* : 279.

JERMYN, M. A.; ISHERWOOD, F. A., 1949: *Biochem. J. 44* : 402.

LAMBERT, M.; NEISH, A. C., 1950: *Canad. J. Res. 28B* : 83.

SHORLAND, F. B., 1944: *Nature. 153* : 168.

———, 1953: *J. Sci. Food Agric. 4* : 497.

NEW ZEALAND
JOURNAL OF GEOLOGY AND GEOPHYSICS

Vol. 2, No. 2, May 1959

CONTENTS

Note on New Zealand Species of *Atomodesma* Beyrich. *J. B. Waterhouse* 259
Note on the Occurrence of Manganese in South-eastern Wairarapa. *H. E. Fyfe* and *J. J. Reed* 262
The Tertiary Geology of the Pareora District, South Canterbury. *H. S. Gair* 265
Sea Level Recordings at Scott Base, Antarctica, 1957. *W. J. P. Macdonald* and *A. L. Burrows* 297
The Sub-tropical Convergence in New Zealand Surface Waters. *D. M Garner* 315
Genus *Leptalosia* Dunbar and Condra. *J. B. Waterhouse* 338
A One-dimensional Fourier Investigation of a Soil Montmorillonite. *L. D. Swindale* 342
On Some Offshore Seismic Refraction Profiles in the Cook Strait, Tasman Bay, and Golden Bay Areas of New Zealand. *Charles B. Officer* 350
Paparoa Mine Area, Greymouth Coalfield—Swelling Properties and Reserves of Coal. *R. P. Suggate* 355
Schistose Rocks from St. Heliers Bay, Auckland. *E. J. Searle* 368
Occurrence of Ignimbrite in the Shag Valley, North-east Otago. *A. Steiner, D. A. Brown,* and *A. J. R. White* 380
Radioactive Boulders in Hawks Crag Breccia. *A. Wodzicki* 385
Some Field and Petrographic Features of American and New Zealand Ignimbrites. *R. C. Martin* 394
Petrography of the Whakapapanui Gorge Andesites, Mount Ruapehu. *B. O. O'Shea* 412

NEW ZEALAND
JOURNAL OF AGRICULTURAL RESEARCH

Volume 2, No, 3, June 1959

CONTENTS

Effects of Shading and Defoliation on the Turnover of Root and Nodule Tissue of Plants of *Trifolium repens, Trifolium pratense,* and *Lotus uliginosus.* *G. W. Butler, R. M. Greenwood,* and *Kathleen Soper* 415
Effect of Phosphate Topdressing on a Soil from Andesitic Volcanic Ash: I—Forms of Soil Phosphorus and a Method for their Determination. *W. H. M. Saunders* 427
II—Effect on Distribution of Phosphorus and on Related Chemical Properties. *W. H. M. Saunders* 445
Experiments on the Control of Ripe Spot on Sturmer Apples. *P. J Brook* 463
Effect on Honey Bees of Rogor and Endothion Applied from the Air as Sprays to Brassicas: Trial of M.G.K. Repellent 874. *T. Palmer-Jones, I. W. Forster,* and *G. L. Jeffery* 475
Effect on Honey Bees of DDT and Thiodan Applied from the Air as Sprays to Chou Moellier. *T. Palmer-Jones, I. W. Forster,* and *G. L. Jeffery* 481
Pasture Management Trials on Unploughable Hill Country at Te Awa: II—Results for 1951–57. *F. E. T Suckling* 488
Fungal Leaf-spot Diseases of Cocksfoot (*Dactylis glomerata* L.) in the Manawatu: III—Eyespot Caused by *Selenophoma donacis* var. *stomaticola* (Bauemel.) Sprague et A. C. Johnson, and Scald Caused by *Rhyncosporium orthosporum* Caldwell. *G. C. M. Latch* and *H. T. Wenham* 544
The Effects of Iodine and Thyroxine Administration on the Romney Crossbred Ewe. *Ballinda J. Myers* and *D. A. Ross* 552
Ovulatory Activity in Mature Romney Ewes in Otago. *R. L W. Averill* 575
Weather Conditions Associated with Outbreaks of Facial Eczema. *K. J. Mitchell, T. O. Walshe,* and *N. G. Robertson* 584
Pollen Sterility in Pukekohe Longkeeper Onions. *D. E. Yen* 605
Incidence and Parasitism of Insect Pests of Cruciferous Crops in the North Island—Evaluation of Data, 1955–58 Seasons. *D. H. Todd* 613
Photosensitivity Diseases in New Zealand: XVI: Improved Procedure for the Beaker Test for Facial-eczema Toxicity. *Jean Sandos, N. T. Clare,* and *E. P. White* 623
Comparison of Faecal Pigments and Faecal Nitrogen as Digestibility Indicators in Grazing Cattle Studies. *W. K. Kennedy, A. H. Carter,* and *R. J. Lancaster* 627

NEW ZEALAND JOURNAL OF SCIENCE

Volume 2, No. 2, June 1959

CONTENTS OF THIS ISSUE

A Study of Home Range in a Feral Goat Herd. *Thane Riney* and *Graeme Caughley* 157

Biological and Chemical Changes following Scrub Burning on a New Zealand Hill Soil: Part 2—Changes in Soil pH. *R. B. Miller* and *M. FitzPatrick* 171

The Air Pollution Problem in Christchurch, New Zealand. *L. Wilkinson* 182

Sampling of Tidal Waters. *L. Wilkinson* 196

Toxicity of Some Arsenical Wood-preservatives to the Common House Borer, *Anobium punctatum* de Geer. *K. M. Harrow* 208

Constituents of *Phyllocladus glaucus*. *E. G. Brooker* 212

The Solubilization of "Insoluble" Phosphates: Part 5—The Action of Some Organic Acids on Iron and Aluminium Phosphates. *H. W. Johnston* 215

An Automatic Apparatus for the Lundegardh Method of Analysis. *J. E. Allan* and *O. E. Clinton* 219

The Extractives of *Vitex lucens* T. Kirk: Part 2—The Leaves and Bark. *R. C. Cambie* 230

Preliminary Flight Records of Diptera Taken with a Modified Rothamsted Light Trap Operated at Paiaka. *R. A. Cumber* and *R. A. Harrison* 237

Leaf Extractives of *Pomaderris elliptica* Labill. *B. F. Cain* and *R. C. Cambie* 240

A Leaching Study of the Buller Gorge Uranium Ore. *R. M. Carr* 244

The Constituents of *Phebalium nudum* Hook.: Part 2—Alkaloids of the Wood. *R. C. Cambie* 254

Wood Extractives of *Aristotelia serrata*. *R. C. Cambie* 257

Separation and Identification of Food Colours. *Alison C. Cooke* 260

Diphenylamine Residues on Apples: Effect of Different Diphenylamine Treatments. *Helen E. Harvey* and *P. J. Clark* 266

A Note on the Acetone-Soluble Lipids of Forage Grasses and Clovers. *R. O. Weenink* 273

SUBSCRIPTIONS.—Subscriptions will be accepted only on advance payment and only for a full calendar year. Price: 20s. per annum; single copy 5s.; post free (surface mail). Published quarterly, March, June, September, and December. Subscriptions should be forwarded to the Publications Officer, Department of Scientific and Industrial Research, P.O. Box 8018, Wellington, New Zealand. Cheques should be made payable to the Department of Scientific and Industrial Research, and if drawn on banks outside Wellington, must have exchange added. Subscribers are requested to give their name and full postal address.

This Journal may also be ordered through The High Commissioner for New Zealand, 415 Strand, London W.C.2, or through any bookseller.

HARRY H. TOMBS LTD., THE WINGFIELD PRESS, WELLINGTON 1250/6/59